



**HAL**  
open science

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

T.A. N'guyen, S. Lejeunes, D. Eyheramendy, Adnane Boukamel

## ► To cite this version:

T.A. N'guyen, S. Lejeunes, D. Eyheramendy, Adnane Boukamel. A thermodynamical framework for the thermo-chemo-mechanical couplings in soft materials at finite strain.. *Mechanics of Materials*, 2016, 10.1016/j.mechmat.2016.01.008 . hal-01266697

**HAL Id: hal-01266697**

**<https://hal.science/hal-01266697>**

Submitted on 18 Apr 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

T.A. N'Guyen<sup>a</sup>, S. Lejeunes<sup>b,\*</sup>, D. Eyheramendy<sup>b</sup>, A. Boukamel<sup>c</sup>

<sup>a</sup>*Da Nang University, Da Nang, Vietnam*

<sup>b</sup>*LMA, Centrale Marseille, CNRS, UPR 7051, Aix-Marseille Univ, F-13402 Marseille Cedex 20, France*

<sup>c</sup>*IRT Railenium, LAMIH, Univ. Valenciennes, F-59300 Famars, France*

---

## Abstract

This paper focus on the modeling of thermo-chemo-mechanical behaviors for soft materials (polymer, rubber, ...) that can exhibit large strain in a rigorous thermodynamical framework. As an application it is considered the case of a thermo-viscoelastic material that can undergo chemical reactions which are described by a kinetic approach. Simple idealized and homogeneous numerical tests are considered and illustrate the availability of this framework to take into account reciprocal coupling between each physics.

*Key words:* polymer, rubber, thermodynamics, irreversible processes

---

## 1. Introduction

Thermo-chemo-mechanical couplings in soft materials (polymers, rubbers, ...) are an important topic that is linked to many different industrial applications. The most evident one concerns the processing of these materials. A precise simulation of material processing can be of great interest to optimize the process, to predict residual strain/stress due to process, to anticipate material heterogeneities (different grade of material due to different chemical states). Another application concerns the prediction of the behavior of industrial parts submitted to severe operating conditions (in aeronautics or spatial applications for instance). In these applications: thermal and chemical aging can be coupled to mechanical damage phenomena. Concerning modelisation, the thermodynamic of irreversible processes is the main basic tool to address these problematics. The pioneer work of Prigogine and co-authors is very important as it allows the interpretation and the modelisation of chemical reactions in the context of irreversible processes (see for instance Prigogine (1968)). Prigogine has considered that a thermodynamical system can be described by classical state variables (temperature, volume,...) and by supplementary ones which are the extend of reactions in the case of reactive systems. Thermodynamical energy potential (Gibbs or Helmholtz free energy) are then dependent on these new thermodynamical variables. Chemical thermodynamical forces can be defined, called affinity, and linked to earlier work of De Donder (1928). The second law of thermodynamic (entropy production) can be satisfied as these chemical thermodynamical forces derive from the thermodynamical potential of energy. The generalisation of these fundamental concepts to the case of continuum mechanic can be done in a straightforward manner by considering the concept of local state and the introduction of internal variables (see Germain et al. (1983) and reference therein). Therefore all the thermodynamical variables are function of time and position. Applying Onsager reciprocity concept (see Onsager (1931)) or using the convex framework of standard generalized materials (see Halphen and Nguyen (1975)) evolution equations for chemistry or mechanical irreversibilities can be established from the definition of a thermodynamical energy potential and eventually from a pseudo potential of dissipation (in the context of standard generalized materials). These general tools has been used by many authors in the literature in the context of soft material subjected to

---

\*Corresponding author

*Email addresses:* lejeunes@lma.cnrs-mrs.fr, tel: 033491054382, fax: 033491712866 (S. Lejeunes)

chemical reactions. Gigliotti and Grandidier (2010); Gigliotti et al. (2011) has proposed a chemo-mechanical coupled model in the context of elastic behavior with several reactions for a thermo-oxydation process in polymer matrix. They also consider the diffusion of species inside the materials to predict aging. In Lion and Höfer (2007); Mahnken (2013) one can find thermo-chemo-mechanical models for the curing of polymer. These models take into account of mechanical, thermal and chemical deformations (dilatation and shrinkage) in a thermo-viscoelastic context. The chemistry is phenomenologically described by a kinetic approach. André and Wriggers (2005) has proposed a thermo-chemo-mechanical model in small strain to simulate the vulcanization of rubber materials. The mechanical behavior is assumed to be elasto-visco-plastic and two phenomenological chemical reactions are considered to describe the vulcanization process. In Kannan and Rajagopal (2011), the authors have developed a framework in finite strain that is applied to vulcanization of rubbers in a viscoelastic context with several chemical reactions.

In this contribution, we propose a rigorous thermodynamical framework that can be used as a basis of development for thermo-chemo-mechanical models. As previously mentioned the basic tools are the thermodynamics of irreversible processes and the local state hypothesis. As already done by some authors, we assume that the volume variation is decomposed in a thermal part (dilation) a chemical part (shrinkage) and a mechanical part (compressibility). Hydrostatic pressure is therefore directly related to the chemical, mechanical and thermal states. This decomposition also implies a coupling of the heat capacity and the chemical evolution upon pressure or volume variation. A kinetic (phenomenological) description of chemistry is chosen. However, due to the fact that mechanical parameters (modulus) and volume variation are dependent on the chemical state, the thermodynamical chemical force is also directly dependent on the mechanical state. The hydrostatic pressure and deviatoric strain can therefore have a favorable or a unfavorable effect on chemical evolution. The main originality of this paper lies in the following points. First, it is proposed a new form of chemical potential of energy, this potential takes into account of an initiation temperature under which no reactions take place and energy is stored as heat. This potential is defined so as to have a clear definition and admissible form of the heat capacity. Second, the chemical evolution that is associated to this potential naturally takes into account of the influence of the mechanical state. It is proposed a new evolution law for chemistry that is inspired from visco-plasticity behavior: the chemical evolution rate is assumed to be null if the thermodynamical force becomes negative (therefore chemical reversion is not allowed) and a chemical viscosity parameter is introduced. This parameter allows the balancing of mechanical influence on chemical evolution.

The paper is organised as follows: the general thermodynamical framework and conservation equations are presented in a first section. As an application it is derived a phenomenological thermo-chemo-visco-elastic model in a second section. This model is general and can be applied to different problematic. In a third section, some simple idealized examples are provided. These examples illustrate both the capability of the proposed model to be applied to different problematic (aging or material processing) and the influence of some material parameters on the reciprocal couplings. In the last section some remarks are addressed to conclude.

## 2. Thermodynamical framework

### 2.1. Definition of a chemical internal variable

In this work, it is considered a solid body submitted to thermo-mechanical loadings. This body is viewed as a closed<sup>1</sup> thermodynamical continuum system and therefore no mass exchange with the outside can occur. Furthermore as classically assumed neither creation nor destruction of mass is allowed. Let us assumed that the initial configuration (at  $t = 0$ ) is defined by a stress and heat flux free state. In this configuration the chemical species are in equilibrium: the reaction rates are null in this state. Using the classical continuum mechanics point of view, the body can be considered as a continuum of material points that are defined by an initial position  $\mathbf{X}$  and a current position  $\mathbf{x}$  in an euclidean space. The material point can be viewed as

---

<sup>1</sup>Chemical reactions in soft material often involve matter (gaz) diffusion and therefore the problem should be considered as on open thermodynamical system, however we neglected this effect in this work.

an infinitesimal element of volume and it can be defined the current material density  $\rho(\mathbf{x}, t)$ , which evolves in times as the volume evolves (the initial density is denoted  $\rho_0$ ). The closed system hypothesis leads to:

$$\dot{\rho} + \rho \operatorname{div}(\mathbf{v}) = 0 \quad (1)$$

where  $\operatorname{div}(\mathbf{v})$  is the eulerian divergence of the velocity of the material point and  $\dot{\rho}$  is the total time derivative (so called material time derivative<sup>2</sup>) of the density. Assuming that this infinitesimal element of volume is a mixture of all chemical species that compose the material, one can defined the current mass concentration of the  $i^{\text{th}}$  species relative to the current infinitesimal volume (of the mixture), denoted  $\rho_i(\mathbf{x}, t)$ . In the case of null diffusion of species inside the body (i.e. no relative velocity of one species from another) the mass conservation is also defined from:

$$\begin{cases} \dot{\rho}_i + \rho_i \operatorname{div}(\mathbf{v}) = m_i & i = 1, 2, \dots, n \\ \sum_{i=1}^n m_i = 0 \end{cases} \quad (2)$$

where  $m_i(\mathbf{x}, t)$  is the rate of production of mass of the  $i^{\text{th}}$  species per unit of current volume of mixture. Knowing the molar mass of each species, denoted  $\mathcal{M}_i$  equations 2 can be rewritten in terms of volume concentration (mole per unit of current volume) denoted  $Y_i = \rho_i/\mathcal{M}_i$ :

$$\begin{cases} \dot{Y}_i + Y_i \operatorname{div}(\mathbf{v}) = \frac{m_i}{\mathcal{M}_i} & i = 1, 2, \dots, n \\ \sum_{i=1}^n m_i = 0 \end{cases} \quad (3)$$

As already mentioned by Kannan and Rajagopal (2011) in finite strain it is not a good idea to consider  $Y_i(\mathbf{x}, t)$  as thermodynamical variables that characterize the chemical state because volume variation leads to a change in concentration (in terms of volume). Following aforementioned authors, we prefer to consider  $n_i$  the number of mole of the  $i$ th species per unit of mass of the mixture:  $n_i(\mathbf{x}, t) = Y_i/\rho = \rho_i/(\rho\mathcal{M}_i)$ . Inserting this definition in 3 and using 1, the mass balance becomes:

$$\sum_{i=1}^n \dot{n}_i \mathcal{M}_i = 0 \quad (4)$$

Therefore only  $n - 1$  variables are sufficient to describe fully the chemical state. If the reactive scheme is known and if this reactive scheme implies  $r$  stoichiometric reactions (with the stoichiometric ratios  $\nu_{ir}$ ), the extent  $\zeta_r$  of the  $r$ th reaction can be defined from:

$$\zeta_r(\mathbf{x}, t) = \frac{n_i^r(\mathbf{x}, t) - n_i^r(\mathbf{X}, 0)}{\nu_{ir}} \quad \forall i, \quad r = 1..m \quad (5)$$

where  $n_i^r(\mathbf{x}, t)$  is the molar concentration of the  $i$ th species for the  $r$ th reaction per unit of mass of the mixture. Finally if both the initial concentration and the stoichiometric coefficients are known the chemical state can be defined by only  $r$  independant variables that describe the advance of reactions.

In this paper, it is only considered one reaction<sup>3</sup> and the chemical state is defined by the following normalized concentration (chemical conversion):

$$\xi(\mathbf{x}, t) = \frac{n_{vu}^1(\mathbf{x}, t) - n_{vu}^1(\mathbf{X}, 0)}{n_{vumax}^1} \quad (6)$$

where  $n_{vu}^1(x, t)$  is the current molar concentration of the product of interest (in the case of material processing this could be the vulcanized or polymerized product) and  $n_{vumax}^1$  is the maximum attainable concentration. The previously defined chemical conversion is chosen to be a thermodynamical internal variable in the following.

<sup>2</sup>derivative of quantity upon time holding initial position constant:  $\dot{\rho} = (\partial\rho(\mathbf{x}, t)/\partial t)_{\mathbf{X}}$

<sup>3</sup>The proposed thermodynamical framework can be easily extended to more complex reacting systems: one has to define at least the same number of internal variables that the number of reactions.

## 2.2. Kinematic

To define kinematic, it is assumed that the motion of all the material points of the body is described by a bijective vectorial function  $\chi(X, t)$  such that:  $\mathbf{x} = \chi(\mathbf{X}, t)$ . The transformation gradient  $\mathbf{F}(\mathbf{X}, t)$  is therefore defined by  $\mathbf{F} = \partial\chi/\partial\mathbf{X}$ . Following Flory (1961), the transformation is split into volumetric and isochoric part:

$$\mathbf{F} = (J^{1/3}\mathbf{1}) \cdot \bar{\mathbf{F}} \quad (7)$$

where  $J = \det\mathbf{F}$  is the volume variation and  $\mathbf{1}$  the identity tensor. It is assumed that the volume variation can result from three independent terms: the mechanical compressibility  $J_m$ , the thermal dilatation  $J_\Theta$  and the chemical shrinkage  $J_\xi$ :

$$J = J_m J_\Theta J_\xi \quad (8)$$

The volume variation terms are defined from the following relations:

$$J_\Theta = 1 + \alpha(\Theta - \Theta_0) \quad (9)$$

$$J_\xi = 1 + \beta g(\xi) \quad (10)$$

$$J_m = J(J_\xi J_\Theta)^{-1} \quad (11)$$

where  $\alpha$  and  $\beta$  are respectively the thermal expansion and chemical shrinkage coefficients,  $\Theta_0$  is the temperature in the initial configuration,  $g$  is a shrinkage function. For the sake of simplicity, the thermal dilatation is assumed as linear (eq. 9). More complex expressions for the thermal dilatation can be considered that depend on the material composition and on the temperature range of the desired application (see for instance Holzapfel and Simo (1996) who have proposed an exponential form). The linearized form of the thermal dilatation is commonly assumed in the case of small thermal variations. However for some materials this hypothesis seems valuable for a large range of temperatures (far from the glass transition temperature). For instance, figure 1 show the evolution of density of a partially hydrogenated poly(acrylonitrile-co-1,3-butadiene) upon temperature for various density of cross-links.

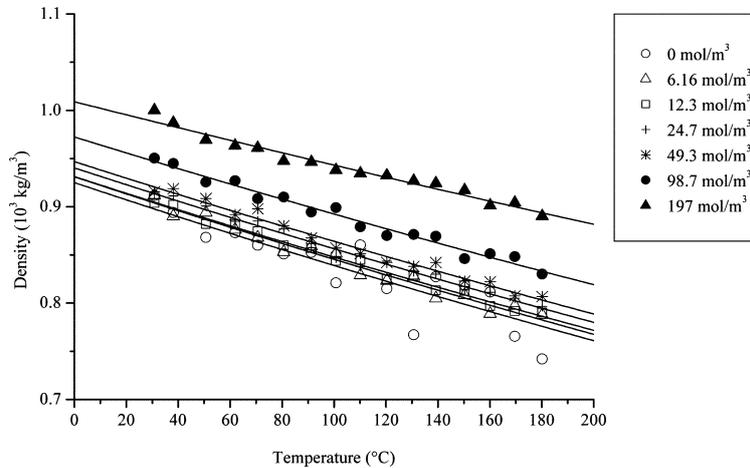


Figure 1: Dependence of the density of HPAB polymer with different degrees of cure on temperature. The legend shows the concentration of cross-links. Issued from Likozar and Krajnc (2011)

To describe inelastic effects an intermediate configuration is introduced and the isochoric transformation gradient is classically decomposed with the following multiplicative split:

$$\bar{\mathbf{F}} = \bar{\mathbf{F}}_e \cdot \bar{\mathbf{F}}_i \quad (12)$$

where  $\bar{\mathbf{F}}_i$  represents the inelastic transformation and  $\bar{\mathbf{F}}_e$  represents elastic one. This decomposition implicitly assumes that inelastic flows are incompressible.

### 2.3. Clausius-Duhem inequality

It is chosen in the following to consider the Helmholtz free specific energy to characterize thermodynamical states. This potential of energy is classical adopted by mechanic whereas chemists are more familiar with Gibbs potential. It is therefore defined  $\psi$  the Helmholtz free specific energy:

$$\psi = e - \Theta s \quad (13)$$

where  $e$  is the specific internal energy and  $s$  is the specific entropy. Combining the first and second laws of thermodynamics together with the previous expression, one can obtain the Clausius-Duhem inequality. In an Eulerian configuration, it can be written as:

$$\phi = \boldsymbol{\sigma} : \mathbf{D} - \rho \dot{\psi} - \rho s \dot{\Theta} - \mathbf{q} \cdot \frac{\text{grad}_{\mathbf{x}} \Theta}{\Theta} \geq 0 \quad \forall \mathbf{D}, \dot{\Theta}, \mathbf{q} \quad (14)$$

where  $\phi$  stands for the dissipation,  $\boldsymbol{\sigma}(\mathbf{x}, t)$  is the Cauchy stress,  $\mathbf{D} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1}$  the eulerian rate of deformation,  $q(\mathbf{x}, t)$  is the eulerian heat flux,  $\text{grad}_{\mathbf{x}}$  is the eulerian gradient operator. Introducing the left Cauchy-Green deformation  $\bar{\mathbf{B}} = \overline{\mathbf{F}\mathbf{F}^T}$  and  $\bar{\mathbf{B}}_{\mathbf{e}} = \overline{\mathbf{F}_{\mathbf{e}}\mathbf{F}_{\mathbf{e}}^T}$  and assuming that the free energy is a function of  $\bar{\mathbf{B}}, \Theta, J, \bar{\mathbf{B}}_{\mathbf{e}}, \xi$ , it can be obtained:

$$\dot{\psi} = \frac{\partial \psi}{\partial \bar{\mathbf{B}}} : \dot{\bar{\mathbf{B}}} + \frac{\partial \psi}{\partial \bar{\mathbf{B}}_{\mathbf{e}}} : \dot{\bar{\mathbf{B}}}_{\mathbf{e}} + \frac{\partial \psi}{\partial J} \dot{J} + \frac{\partial \psi}{\partial \Theta} \dot{\Theta} + \frac{\partial \psi}{\partial \xi} \dot{\xi} \quad (15)$$

where:

$$\dot{J} = J(\mathbf{1} : \mathbf{D}) \quad (16)$$

$$\dot{\bar{\mathbf{B}}} = \mathbf{L} \cdot \bar{\mathbf{B}} + \bar{\mathbf{B}} \cdot \mathbf{L}^T - \frac{2}{3}(\mathbf{1} : \mathbf{D})\bar{\mathbf{B}} \quad (17)$$

$$\dot{\bar{\mathbf{B}}}_{\mathbf{e}} = \mathbf{L} \cdot \bar{\mathbf{B}}_{\mathbf{e}} + \bar{\mathbf{B}}_{\mathbf{e}} \cdot \mathbf{L}^T - 2\bar{\mathbf{V}}_{\mathbf{e}} \cdot \bar{\mathbf{D}}_{\mathbf{i}}^{\circ} \cdot \bar{\mathbf{V}}_{\mathbf{e}} - \frac{2}{3}(\mathbf{1} : \mathbf{D})\bar{\mathbf{B}}_{\mathbf{e}} \quad (18)$$

with  $\bar{\mathbf{V}}_{\mathbf{e}}$  is the pure deformation coming from the polar decomposition of  $\bar{\mathbf{F}}_{\mathbf{e}} = \bar{\mathbf{V}}_{\mathbf{e}} \cdot \bar{\mathbf{R}}_{\mathbf{e}}$ ,  $\bar{\mathbf{D}}_{\mathbf{i}}^{\circ}$  is the objective rate of inelastic deformation, defined from:  $\bar{\mathbf{D}}_{\mathbf{i}}^{\circ} = \bar{\mathbf{R}}_{\mathbf{e}} \cdot \bar{\mathbf{D}}_{\mathbf{i}} \cdot \bar{\mathbf{R}}_{\mathbf{e}}^T$ .

Inserting equations (16), (17), (18) in (15) and putting the result in (14) and regrouping terms, we have:

$$\begin{aligned} \phi = & \left( \boldsymbol{\sigma} - 2\rho \left( \bar{\mathbf{B}} \cdot \frac{\partial \psi}{\partial \bar{\mathbf{B}}} + \bar{\mathbf{B}}_{\mathbf{e}} \cdot \frac{\partial \psi}{\partial \bar{\mathbf{B}}_{\mathbf{e}}} \right)^{\text{D}} - \rho J \frac{\partial \psi}{\partial J} \mathbf{1} \right) : \mathbf{D} + 2\rho \left( \bar{\mathbf{B}}_{\mathbf{e}} \cdot \frac{\partial \psi}{\partial \bar{\mathbf{B}}_{\mathbf{e}}} \right)^{\text{D}} : \bar{\mathbf{D}}_{\mathbf{i}}^{\circ} \\ & - \rho \left( s + \frac{\partial \psi}{\partial \Theta} \right) \dot{\Theta} - \rho \frac{\partial \psi}{\partial \xi} \dot{\xi} - \frac{\text{grad}_{\mathbf{x}} \Theta}{\Theta} \cdot \mathbf{q} \geq 0 \end{aligned} \quad (19)$$

To proceed further, it is made the following hypothesis: entropy is fully defined from the free specific energy variation and there are no dissipation for the thermodynamical force associated with the thermodynamical flux  $\mathbf{D}$ . This leads to:

$$s = -\frac{\partial \psi}{\partial \Theta} \quad (20)$$

$$\boldsymbol{\sigma} = \underbrace{2\rho \left( \bar{\mathbf{B}} \cdot \frac{\partial \psi}{\partial \bar{\mathbf{B}}} \right)^{\text{D}}}_{\boldsymbol{\sigma}_{eq}} + \underbrace{2\rho \left( \bar{\mathbf{B}}_{\mathbf{e}} \cdot \frac{\partial \psi}{\partial \bar{\mathbf{B}}_{\mathbf{e}}} \right)^{\text{D}}}_{\boldsymbol{\sigma}_{neq}} + \underbrace{\rho J \frac{\partial \psi}{\partial J} \mathbf{1}}_{\boldsymbol{\sigma}_{vol}} \quad (21)$$

It remains the following terms in the dissipation:

$$\phi = \overbrace{2\rho \left( \bar{\mathbf{B}}_{\mathbf{e}} \cdot \frac{\partial \psi}{\partial \bar{\mathbf{B}}_{\mathbf{e}}} \right)^{\text{D}} : \bar{\mathbf{D}}_{\mathbf{i}}^{\circ}}^{\phi_m} + \overbrace{\left( -\rho \frac{\partial \psi}{\partial \xi} \dot{\xi} \right)}^{\phi_{\xi}} + \overbrace{\left( -\frac{\text{grad}_{\mathbf{x}} \Theta}{\Theta} \right) \cdot \mathbf{q}}^{\phi_{\Theta}} \geq 0 \quad (22)$$

where  $\phi_m$  is the intrinsic dissipation,  $\phi_\xi$  the chemical dissipation and  $\phi_\theta$  the thermal dissipation. It is assumed that  $\phi_m$ ,  $\phi_\xi$  and  $\phi_\theta$  are independently positives. Interesting readers can refer to Germain et al. (1983) and references therein for a general discussion on thermodynamics of local state models. From eq. (22), it can be defined a mechanical thermodynamical force  $\sigma_i = 2\rho(\bar{\mathbf{B}}_e \cdot \partial\psi/\partial\bar{\mathbf{B}}_e)^D$ , a chemical force  $\mathcal{A}_\xi = -\rho\partial\psi/\partial\xi$  and a heat force  $\mathcal{A}_\Theta = -\text{grad}_{\mathbf{x}}\Theta/\Theta$ .

#### 2.4. Heat equation

The heat equation can be obtained from the first thermodynamical principle (energy conservation), which takes the following local form in the eulerian configuration:

$$\rho\dot{e} = \sigma : \mathbf{D} + \rho r - \text{div}_{\mathbf{x}}\mathbf{q} \quad (23)$$

Where  $r$  is a volumetric heating source term (defined by unit of volume). The material time derivative of eq. (13) leads to:

$$\dot{e} = \dot{\psi} + s\dot{\Theta} + \dot{s}\Theta \quad (24)$$

using eq (24) in eq (23), one can obtain:

$$\rho\dot{s}\Theta = \sigma : \mathbf{D} + \rho r - \text{div}_{\mathbf{x}}\mathbf{q} - \rho\dot{\psi} - \rho s\dot{\Theta} \quad (25)$$

The material time derivative of the free energy is given by eq (15) and using eqs (16), (17), (18), (20) in (25):

$$\rho\dot{s}\Theta = \phi_m + \phi_c + \rho r - \text{div}_{\mathbf{x}}\mathbf{q} \quad (26)$$

The material time derivative of the entropy is obtained from eq (20):

$$\dot{s} = -\frac{\partial^2\psi}{\partial\theta^2}\dot{\Theta} - \frac{\partial^2\psi}{\partial\theta\partial\xi}\dot{\xi} - 2\left(\bar{\mathbf{B}} \cdot \frac{\partial^2\psi}{\partial\Theta\partial\bar{\mathbf{B}}} + \bar{\mathbf{B}}_e \cdot \frac{\partial^2\psi}{\partial\Theta\partial\bar{\mathbf{B}}_e}\right)^D : \mathbf{D} + 2\left(\bar{\mathbf{B}}_e \frac{\partial^2\psi}{\partial\Theta\partial\bar{\mathbf{B}}_e}\right)^D : \bar{\mathbf{D}}_i^\circ - J\frac{\partial^2\psi}{\partial\Theta\partial J}(\mathbf{1} : \mathbf{D}) \quad (27)$$

Finally, the heat equation is obtained by replacing eq (27) in eq (26):

$$\rho C\dot{\Theta} = \phi_m + \phi_c + l_m + l_c + \rho r - \text{div}_{\mathbf{x}}\mathbf{q} \quad (28)$$

where  $C$  is the specific heat capacity which is defined from:

$$C = -\Theta\frac{\partial^2\psi}{\partial\theta^2} \quad (29)$$

the coupling terms  $l_m$  and  $l_c$  are defined from:

$$l_m = \Theta\frac{\partial\sigma}{\partial\Theta} : \mathbf{D} - \Theta\frac{\partial\sigma_{neq}}{\partial\Theta} : \bar{\mathbf{D}}_i^\circ \quad (30)$$

$$l_c = -\Theta\frac{\partial\mathcal{A}_\xi}{\partial\Theta}\dot{\xi} \quad (31)$$

### 3. Application: a thermo-chemo-visco phenomenological model

One can consider the specific free energy splitting into mechanical, thermal and chemical parts as:

$$\psi = \psi_m(\bar{\mathbf{B}}, \bar{\mathbf{B}}_e, \xi, \Theta, J) + \psi_\Theta(\Theta) + \psi_\xi(\Theta, \xi) \quad (32)$$

This decomposition is based on the following ideas: (i) the mechanical behavior is strongly dependent on chemical and thermal state even if the behavior is elastic, (ii) without mechanical deformations or mechanical stresses the chemical free energy will mainly depend on the chemical state and on the temperature (classical thermo-kinetic approach), (iii) in a purely thermal process free energy depends only on temperature. Using the previous decomposition leads to an additive splitting of the entropy and eventually to the specific heat capacity splitting:

$$s = -\frac{\partial\psi}{\partial\Theta} = s_m + s_\Theta + s_\xi \quad C = -\Theta\frac{\partial^2\psi}{\partial\Theta^2} = C_m + C_\Theta + C_\xi \quad (33)$$

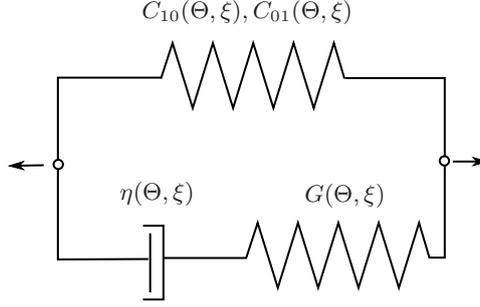


Figure 2: A visco-elastic model

### 3.1. mechanical part

Without loss of generality it is chosen the very simple Zener viscoelastic model for the mechanical behavior. The model is schematized on the figure 2. The mechanical free energy is decomposed into an equilibrium, a non-equilibrium and a volumetric part:

$$\psi_m(\bar{\mathbf{B}}, \bar{\mathbf{B}}_e, \xi, \Theta, J) = \psi_{eq}(\bar{\mathbf{B}}, \xi, \Theta) + \psi_{neq}(\bar{\mathbf{B}}_e, \xi, \Theta) + \psi_{vol}(J, \xi, \Theta) \quad (34)$$

The equilibrium and non-equilibrium free energy are based on Mooney-Rivlin and neo-Hookean hyperelastic model:

$$\rho_0 \psi_{eq} = C_{10}(\Theta, \xi)(I_1(\bar{\mathbf{B}}) - 3) + C_{01}(\Theta, \xi)(I_2(\bar{\mathbf{B}}) - 3) \quad (35)$$

$$\rho_0 \psi_{neq} = G(\Theta, \xi)(I_1(\bar{\mathbf{B}}_e) - 3) \quad (36)$$

where  $I_1(\bullet)$  and  $I_2(\bullet)$  are the first and second invariant of the tensorial argument  $(\bullet)$ , defined by  $I_1(\bullet) = \text{tr}(\bullet)$  and  $I_2(\bullet) = 1/2(I_1(\bullet)^2 - \text{tr}(\bullet^2))$ . The material parameter  $C_{10}$ ,  $C_{01}$  and  $G$ , are assumed to depend both on temperature and chemical state. The volumetric part is assumed to be related only to compressibility and the compressibility modulus  $K_v$  is assumed to be independent of the thermal and chemical state:

$$\rho_0 \psi_{vol} = \frac{K_v}{2}(J_m - 1)^2 = \frac{K_v}{2}\left(\frac{J}{J_\Theta J_\xi} - 1\right)^2 \quad (37)$$

The stresses are therefore expressed as:

$$\begin{cases} \boldsymbol{\sigma}_{eq} = 2C_{10}(\Theta, \xi)J^{-1}\bar{\mathbf{B}}^D + 2C_{01}(\Theta, \xi)J^{-1}(I_1(\bar{\mathbf{B}})\bar{\mathbf{B}} - \bar{\mathbf{B}}^2)^D \\ \boldsymbol{\sigma}_{neq} = 2G(\Theta, \xi)J^{-1}\bar{\mathbf{B}}_e^D \\ \boldsymbol{\sigma}_{vol} = K_v(J_m - 1)J_\Theta^{-1}J_\xi^{-1}\mathbf{1} = p\mathbf{1} \end{cases} \quad (38)$$

The visco-elastic behavior is assumed to be described by the following flow rule:

$$\bar{\mathbf{D}}_i^o = \frac{2}{\eta(\Theta, \xi)} \left( \bar{\mathbf{B}}_e \cdot \frac{\partial \psi}{\partial \bar{\mathbf{B}}_e} \right)^D = \frac{2G(\Theta, \xi)}{\eta(\Theta, \xi)} \bar{\mathbf{B}}_e^D \quad (39)$$

where  $\eta(\Theta, \xi)$  is a viscosity parameter.

Using (39) in (18), it is obtained the following evolution equation (classical Maxwell viscosity):

$$\dot{\bar{\mathbf{B}}}_e = \mathbf{L} \cdot \bar{\mathbf{B}}_e + \bar{\mathbf{B}}_e \cdot \mathbf{L}^T - \frac{2}{3}(\mathbf{1} : \mathbf{L})\bar{\mathbf{B}}_e - \frac{1}{\tau(\Theta, \xi)} \bar{\mathbf{B}}_e^D \cdot \bar{\mathbf{B}}_e \quad (40)$$

where  $\tau(\Theta, \xi) = \eta(\Theta, \xi)/4G(\Theta, \xi)$  is a characteristic time of viscosity. If the dependency of  $C_{01}$ ,  $C_{10}$  upon temperature is assumed to be linear, the mechanical contribution to the heat capacity is only given by:

$$\rho_0 C_m = \Theta K_v \alpha^2 (2 - 3J_m) J J_\Theta^{-3} J_\xi^{-1} - \Theta \frac{\partial^2 G}{\partial \Theta^2} (I_1(\bar{\mathbf{B}}_e) - 3) \quad (41)$$

This contribution can be either positive or negative depending on the value of  $J_m$  and the sign of the second derivative of the modulus  $G$ . However,  $C_m$  is usually small compared to  $C_\Theta$ .

### 3.2. Thermal part

For the thermal part of the free energy it is adopted the form proposed by Reese and Govindjee (1997); Behnke et al. (2011) which leads to a linear dependency of heat capacity upon temperature:

$$\rho_0\psi_\Theta(\Theta) = C_0 \left( \Theta - \Theta_0 - \Theta \log \left( \frac{\Theta}{\Theta_0} \right) \right) - C_1 \frac{(\Theta - \Theta_0)^2}{2\Theta_0} \quad (42)$$

An isotropic Fourier transport is assumed for the heat flux in the eulerian configuration:

$$\mathbf{q} = -k_t \text{grad}_{\mathbf{x}} \Theta \quad (43)$$

where  $k_t$  is the thermal conductivity coefficient and it is neglected the dependence of this coefficient upon temperature and chemical state. One can easily verify that the previous heat flux is thermodynamically consistent, *ie.* the mechanical dissipation is always positive independently of the thermodynamic state.

The contribution of the thermal part to the heat capacity is therefore:

$$\rho_0 C_\Theta = C_0 + C_1 \frac{\Theta}{\Theta_0} \quad (44)$$

### 3.3. Chemical part

The choice of a free energy for a chemical reactive system within a rigorous thermodynamical framework is not obvious. For well established reactive systems (when stoichiometric equations can be written with a clear reactive scheme), the Gibbs free energy can be written as a function of chemical potentials of each species. For perfect or ideal systems the chemical potentials have simple form which can depend on temperature and hydrostatic pressure. This approach has been used by Kannan and Rajagopal (2011) for the vulcanization of natural rubber. The authors consider a complex reactive scheme in isothermal conditions. In Mahnken (2013), it is proposed to formulate the chemical part of the free energy as a linear function of the chemical conversion and the amount of heat generated during curing. This amount of heat depends on the all history during processing and it is considered as a material parameter in the aforementioned study.

In this work it is proposed a different approach: at constant temperature the free energy has to be the integral of the chemical force for an increment of the chemical conversion. As a kinetic approach is assumed, the chemical force is multiplicatively split into a function of the conversion ( $\xi$ ) and a function of the temperature. The conversion part is inspired by the work of Prime (1973). The temperature part is motivated by the fact that in general it exists a temperature of activation of chemical reactions. Below this temperature no reactions occur and heat is stored by the material. The temperature part also control the thermochemical coupling term in the heat transport equation and eventually the dependency of the heat capacity to the chemical conversion. This two contributions are rarely discussed in the literature but wrong choices may lead to non-physical models. It is proposed to use the following form for the chemical part of the free energy:

$$\rho_0\psi_\xi(\Theta, \xi) = C_2 \left( \Theta_i \log \left( \frac{\Theta}{\Theta_i} \right) \frac{(1 - \xi)^{m+1}}{m + 1} - \Theta_0 \log \left( \frac{\Theta_0}{\Theta_i} \right) \right) \quad (45)$$

where  $C_2$  and  $m$  are material parameter,  $\Theta_i$  is an initiation temperature: below this temperature at a null hydrostatic pressure (pressure of free stress state in the present model) no reaction can occur. The chemical force is therefore given by:

$$\begin{aligned} \mathcal{A}_\xi &= -\rho_0 J^{-1} \frac{\partial \psi_m}{\partial \xi} - \rho_0 J^{-1} \frac{\partial \psi_\xi}{\partial \xi} \\ \rho_0 \frac{\partial \psi_\xi}{\partial \xi} &= -C_2 \Theta_i \log \left( \frac{\Theta}{\Theta_i} \right) (1 - \xi)^m \\ \rho_0 \frac{\partial \psi_m}{\partial \xi} &= \frac{\partial C_{10}}{\partial \xi} (I_1(\bar{\mathbf{B}}) - 3) + \frac{\partial C_{01}}{\partial \xi} (I_2(\bar{\mathbf{B}}) - 3) + \frac{\partial G}{\partial \xi} (I_1(\bar{\mathbf{B}}_e) - 3) - \beta \frac{\partial g}{\partial \xi} J_\xi^{-1} p \end{aligned} \quad (46)$$

The chemical force is therefore coupled to the mechanical state through the dependency of the mechanical parameter upon  $\xi$  and through the hydrostatic pressure. Furthermore the sign of this coupling determine the influence of the mechanics upon chemistry a given state of strain and stress can be favorable or unfavorable (a hydrostatic compression state is *a priori* favorable to a vulcanization process for rubbers or polymerization for polymers).

It is assumed the following evolution equation:

$$\dot{\xi} = k(\Theta) \langle \mathcal{A}_\xi \rangle \quad (47)$$

where  $\langle . \rangle$  are the Mac-Cauley brackets<sup>4</sup>,  $k(\Theta)$  is a kinetic rate term which is here assumed to follow an Arrhenius law:

$$k(\Theta) = A \exp \frac{-E_a}{R\Theta} \quad (48)$$

where  $A$  is a material parameter,  $E_a$  is an activation energy and  $R$  is the ideal gaz constant ( $R = 8.314 J/mol/K$ ). The Mac-Cauley brackets are introduced to guarantee a null or positive chemical evolution<sup>5</sup>.

If one consider a deformation for which  $I1 = I2 = 3$ , the kinetic evolution is therefore defined by:

$$\dot{\xi} = \frac{A}{J} \exp \frac{-E_a}{R\Theta} \left\langle C_2 \Theta_i \log \left( \frac{\Theta}{\Theta_i} \right) (1 - \xi)^m + \beta \frac{\partial g}{\partial \xi} J_\xi^{-1} p \right\rangle \quad (49)$$

It can be seen from the previous equation that if  $\Theta < \Theta_i$  the first term inside the Mac-Cauley Brackets is negative and therefore no reactions can occur if the second term is null (null hydrostatic pressure) or negative (depending on the sign of  $\partial g/\partial \xi$  and the sign of  $p$ ). The relative influence of mechanic under chemical reaction is parametrized by the product  $C_2 \times A$  and  $\beta \times A$ .

Inserting (47) in the expression of  $\phi_\xi$  leads to a straight forward proof of the admissibility of the previous chemical flow rule:

$$\phi_\xi = k(\Theta) \langle \mathcal{A}_\xi \rangle \mathcal{A}_\xi \geq 0 \quad \forall \xi, \Theta, \mathbf{F} \quad (50)$$

The contribution of the chemical free energy to the heat capacity is obtained as follows:

$$\rho_0 C_\xi = -\Theta \frac{\partial^2 \psi_\xi}{\partial \Theta^2} = C_2 \frac{\Theta_i}{\Theta} \frac{(1 - \xi)^{m+1}}{m + 1} \quad (51)$$

This chemical heat capacity is a positive decreasing function of  $\xi$ . It can be seen that the proposed form of the chemical free energy is *a priori* compatible with the idea of a heat energy storage to be released during chemical reactions. In the literature, it can be found that the impact of the chemical evolution upon the specific heat capacity is greatly dependent on the material and the chemical process considered. In Likozar and Krajnc (2011), authors show that the heat capacity of a HPAB polymer has mainly a linear dependency upon temperature and a decreasing behavior upon the formation of chemical bonds in the polymer (this effect is important: 25% of relative influence on the heat capacity from the uncured to the fully cured state). In Dimier (2003) the vulcanisation of a natural rubber with carbon black fillers is considered, the authors show that the heat capacity evolution upon chemical state is very low and could be neglected (for a Natural Rubber with carbon black).

The shrinkage function  $g(\xi)$  must fulfill some restrictions: this function has to be chosen such as  $-1 < g(\xi) \leq 0 \quad \forall \xi$  and  $g(\xi = 0) = 0$  to guaranty that  $0 < J_\xi \leq 1$ . In the present model the following form has been adopted:

$$g(\xi) = \frac{0.367 - \exp^{-(1-\xi)^n}}{0.632} \quad (52)$$

<sup>4</sup> $\langle f \rangle = f$  if  $f > 0$  and  $\langle f \rangle = 0$  if  $f \leq 0$

<sup>5</sup>A negative chemical evolution (reversion) could be thermodynamically admissible, however the authors believe that one have to introduce supplementary mechanisms (reactions or damage) that leads to reversion to be consistent.

where  $n$  is a material parameter that controls the chemical shrinkage function as well as the material parameter  $\beta$  that is the shrinkage coefficient (see eq. (3)). Figure 3 shows the influence of  $n$  on the shrinkage function. It is also assumed in this work that the chemical rate  $\dot{\xi}$ , is identically null when  $\xi = 1$ , therefore  $g'(\xi = 1)$  must be null. This condition is fulfilled if  $n > 1$ .

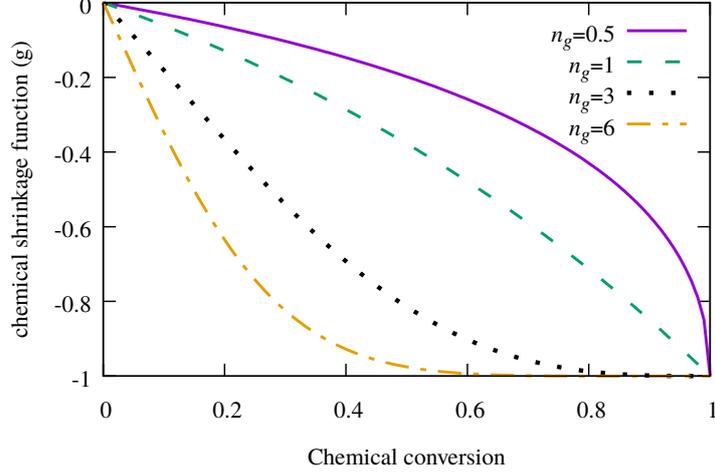


Figure 3: Shrinkage function  $g(\xi)$

#### 4. Numerical simulation for simple homogeneous tests

The material parameters are synthesized in table 1. These parameters have not been identified from a real material however the order of magnitude of most of them are closed from those of a filled rubber material. For the mechanical parameters, it has been adopted the following hypothesis:

- the chemical conversion is assumed to stiffen the mechanical behavior
- far from the glass transition temperature, an increase of the temperature leads to a stiffening effect for the elastic part (parameter  $C_{10}$ ) of the model (entropic elasticity) and to a softening effect for the viscoelastic part (parameter  $G$ ).
- the characteristic time of viscosity:  $\eta/(4G)$ , is a decreasing function of the temperature.

##### 4.1. Exemple 1: cyclic shearing at fixed temperature and fixed chemical conversion

To illustrate the influence of chemical conversion and temperature on the mechanical response, it is considered a cyclic simple shear test. The response is assumed as homogeneous and the deformation gradient is stated as following (thermal dilatation and chemical shrinkage are neglected):

$$\mathbf{F}(t) = \begin{bmatrix} 1 & \gamma(t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \gamma(t) = g \sin(2\Pi ft) \quad (53)$$

where  $f = 1Hz$  is the chosen frequency and  $g$  is the amplitude of the signal. It is also assumed the following form for the viscoelastic Cauchy-Green gradient:

$$\bar{\mathbf{B}}_e(t) = \begin{bmatrix} B_{e11}(t) & B_{e12}(t) & 0 \\ B_{e12}(t) & B_{e22}(t) & 0 \\ 0 & 0 & 1/(B_{e11}(t)B_{e22}(t)) \end{bmatrix} \quad (54)$$

Density	$\rho_0(Kg/m^3)$ 1000			
Thermal part	$\alpha(K^{-1})$ $2.2e^{-4}$	$C_0(J/m^3/K)$ $8e^5$	$C_1(J/m^3/K)$ $1e^6$	$k_t(W/m/K)$ 0.22
Mechanical part	$K_v(Pa)$ $1.0e^9$	$C_{10}(Pa)$ $1.e^6(0.2 + 1.5e^{-3}(\Theta - 273) + 0.35\xi)$		$C_{01}(Pa)$ $1.e^4$
	$\eta(Pa.s)$ $7.3e^3(201 + 1.1e^{-3}(\Theta - 273))$	$G(Pa)$ $1.e^5(0.2 + 2.5\xi) + 8.e^7/(\Theta - 200)$		
Chemical part	$C_2(J/m^3/K)$ $2.0e^5$	$A((Pa.s)^{-1})$ $9.0e^{-4}$	$Ea(J/mol)$ $4.9e^4$	$\Theta_i(K)$ 373
	$n$ 2	$m$ 1.3	$\beta$ 0.03	

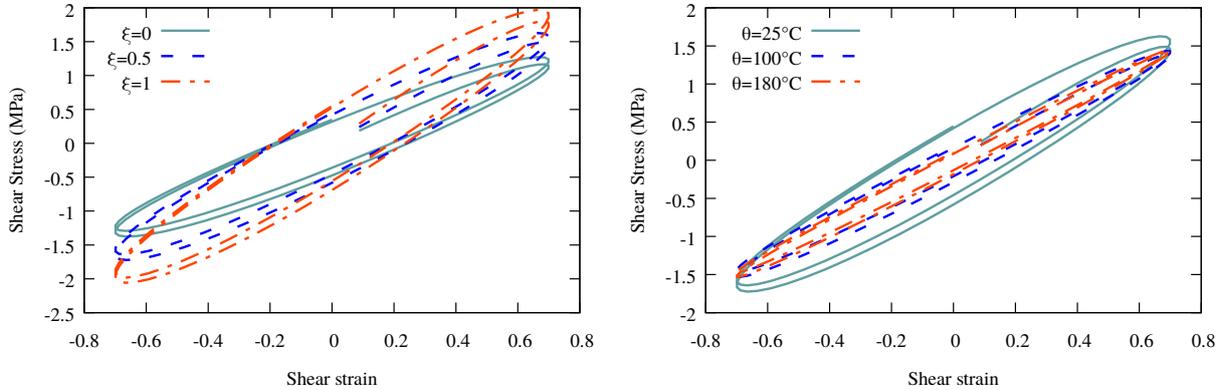
Table 1: Material parameters: mechanical and thermal parts

For this test, the shear stress is fully determined by the material behavior model independently of the equilibrium equation. The equations are:

$$\sigma_{12} = 2\gamma(t)(C_{10}(\Theta, \xi) + C_{01}) + 2G(\Theta, \xi)B_{e12}(t) \quad (55)$$

$$\dot{\bar{\mathbf{B}}}_e = \mathbf{L} \cdot \bar{\mathbf{B}}_e + \bar{\mathbf{B}}_e \cdot \mathbf{L}^T - \frac{1}{\tau(\Theta, \xi)} \bar{\mathbf{B}}_e^D \cdot \bar{\mathbf{B}}_e \quad (56)$$

Using (53) and (54) in (56), one can obtain a system of three differential equation with three unknowns ( $B_{e11}, B_{e12}, B_{e22}$ ). This system is solved using the NDSolve function of Mathematica (Wolfram Research (2014)),  $\Theta$  and  $\xi$  are fixed. The results are synthetized on the figures 4.



(a) Cyclic shear test at  $\Theta=298K$  for various conversion values. Stiffening effect due to chemo-mechanical coupling. (b) Cyclic shear test at  $\xi = 0.5$  for various temperature values. Thermal softening and hysteresis area decreasing due to temperature increase.

Figure 4: Mechanical response to cyclic shear test at constant temperature and constant chemical conversion values.

These results clearly show that the chemical conversion has a stiffening effect on the dynamical mechanical response (at a fixed temperature) and that temperature increase leads to a softer and less dissipative dynamical response (at fixed chemical conversion).

#### 4.2. Example 2: Isothermal case with fixed hydrostatic pressure

It is considered a block of matter in isothermal conditions and submitted to an hydrostatic pressure. The thermal evolution and dilatation effect are neglected. The deformation, the temperature and the chemical

state are assumed to be homogeneous. In this case, the equations of the model become:

$$J_\xi = 1 + \beta g(\xi) \quad (57)$$

$$p = K_v(J_m - 1)J_\xi^{-1} = K_v\left(\frac{J}{J_\xi} - 1\right)J_\xi^{-1} \quad (58)$$

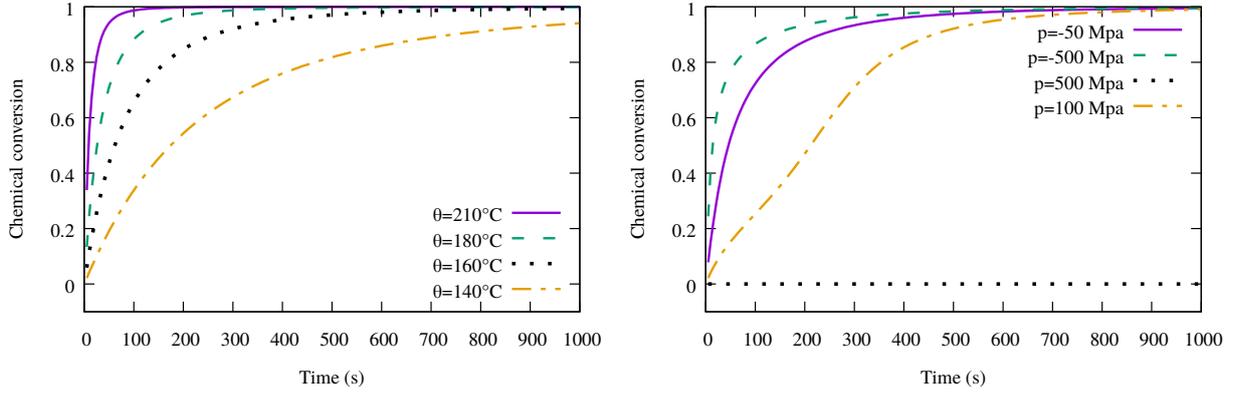
$$\dot{\xi} = \frac{A}{J} \exp\left(\frac{-E_a}{R\Theta}\right) \left\langle C_2 \Theta_i \log\left(\frac{\Theta}{\Theta_i}\right) (1 - \xi)^m + \beta \frac{\partial g}{\partial \xi} J_\xi^{-1}(\xi) p \right\rangle, \quad \xi(t=0) = 0 \quad (59)$$

From eqs (58) and (57) it can be obtained the volume variation as a function of the hydrostatic pressure and the chemical conversion:

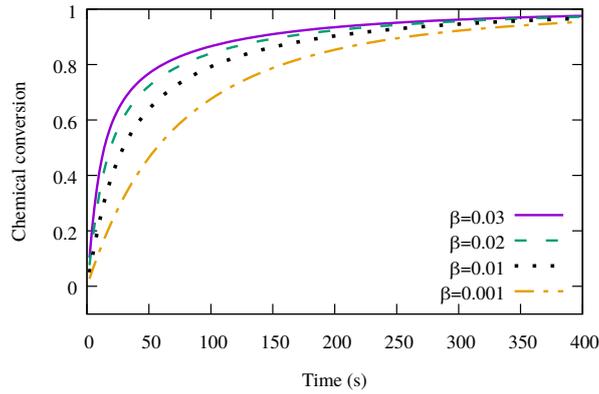
$$J = \frac{p}{K_v} (1 + \beta g(\xi))^2 + (1 + \beta g(\xi)) \quad (60)$$

Considering the case  $p \ll K_v$  this simplify to:  $J = J_\xi = (1 + \beta g(\xi))$ , inserting this result in eq (59) the chemical conversion is therefore defined by:

$$\dot{\xi} = \frac{A \exp\left(\frac{-E_a}{R\Theta}\right)}{1 + \beta g(\xi)} \left\langle C_2 \Theta_i \log\left(\frac{\Theta}{\Theta_i}\right) (1 - \xi)^m + \beta \frac{\partial g}{\partial \xi} (1 + \beta g(\xi))^{-1} p \right\rangle, \quad \xi(t=0) = 0 \quad (61)$$



(a) Isothermal chemical conversion at  $p = 0 \text{ Mpa}$ , effect of the temperature. (b) Isothermal chemical conversion at  $\Theta = 160\text{C}$ , effect of the hydrostatic pressure.



(c) Isothermal chemical conversion at  $\Theta = 160\text{C}$  and  $p = -100 \text{ Mpa}$ , effect of the shrinkage coefficient.

Figure 5: Chemical conversion at fixed temperature and fixed hydrostatic pressure.

By noting  $f(\xi) = -g'(\xi)(1 + \beta g(\xi))^{-1}$  the influence of chemical shrinkage function on kinetic evolution, eq (61) can be written as:

$$\dot{\xi} = \frac{A \exp \frac{-E_a}{R\Theta}}{1 + \beta g(\xi)} \left\langle C_2 \Theta_i \log \left( \frac{\Theta}{\Theta_i} \right) (1 - \xi)^m + \beta f(\xi) p \right\rangle, \quad \xi(t=0) = 0 \quad (62)$$

The previous differential equation is numerically solved with the NDSolve function of Mathematica.

Figures 5 show the response of the model in isothermal condition at fixed temperature. As observed for rubber system, the chemical conversion is very sensitive to the temperature. The influence of the hydrostatic pressure can be clearly observed: hydrostatic compression leads to an acceleration of the conversion contrary to hydrostatic tension that could stop the chemical process when a limit is reached. The relative influence of mechanic on chemistry can be very sensitive to the shrinkage coefficient as can be seen on figure 5(c).

#### 4.3. Example 3: adiabatic case with hydrostatic pressure, application to material processing

In this example it is considered the fictitious case of the vulcanization of a block of rubber. The matter is submitted to a thermal and pressure cycle which is supposed to be representative of rubber curing process. No heat exchange is considered with the outside (adiabatic case) and the temperature is assumed to be homogeneous. Thermal diffusion is neglected however thermal dilatation is taken into account. The deformation is assumed to be homogenous and purely hydrostatic. The figure 6 shows the pressure and heating cycle considered: pressure is first applied linearly at the end of this ramp heating start and is then released. Pressure is kept fixed during chemical conversion followed by a cooling phase. Finally pressure is released to zero. In the following the amplitude values of heat source are the same for each test (max/min value of  $6 \text{ MJ/m}^3$  of initial volume) and different values of hydrostatic pressure amplitude and sign are chosen to illustrate the influence of mechanical couplings.

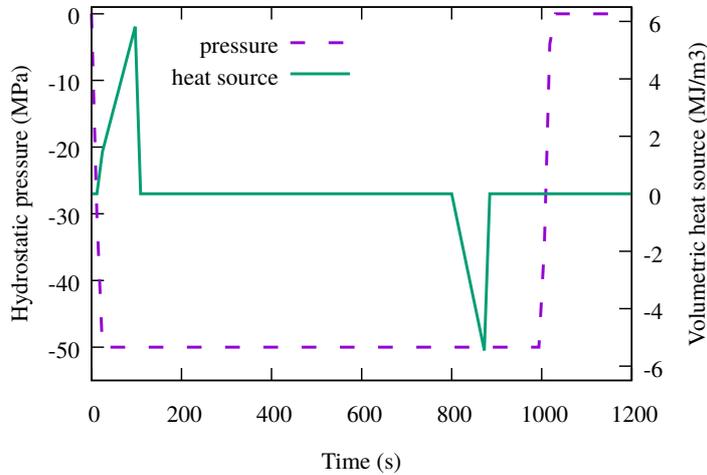


Figure 6: Hydrostatic pressure and volumetric heating cycle.

For this problem as the deformation is purely hydrostatic, the system of equations is reduced to:

$$p = K_v \left( \frac{J}{J_\Theta(\Theta) J_\xi(\xi)} - 1 \right) \frac{1}{J_\Theta(\Theta) J_\xi(\xi)} \quad (63)$$

$$\dot{\Theta} = J \left( \frac{\phi_\xi(\Theta, \xi, J) + l_m(\Theta, \xi, J) + l_c(\Theta, \xi, J) + J^{-1} \rho_0 r}{\rho_0 C(\Theta, \xi, J)} \right), \quad \Theta(t=0) = \Theta_0 \quad (64)$$

$$\dot{\xi} = \frac{A}{J} \exp \frac{-E_a}{R\Theta} \left\langle C_2 \Theta_i \log \left( \frac{\Theta}{\Theta_i} \right) (1 - \xi)^m + \beta \frac{\partial g}{\partial \xi} J_\xi^{-1}(\xi) p \right\rangle, \quad \xi(t=0) = 0 \quad (65)$$

The previous system of equations is resolved numerically with a standard Euler (explicit) method with a small step size ( $dt = 0.2s$ ). Each physics are therefore integrated at the same times with the same scheme (Mathematica is also used for this test).

The results of the numerical simulation are presented on figures 7. It can be made the following observations: - a hydrostatic tension state of stress ( $p = 50Mpa$ ) leads to the smallest chemical conversion and therefore reach the smaller temperature during curing; -the higher the compression the fastest is the chemical evolution and as the reaction is exothermic the higher is the temperature. The competition between thermal dilatation/chemical shrinkage can be clearly seen on the figure that shows the volume variation. The figures 8 show that at the end of curing after cooling with the same amount of volumetric energy than this of heating and after pressure release the final temperature is slightly different than the initial one which is of  $20C$ . The final temperature is also dependent on the hydrostatic pressure applied during curing. The final shrinkage value correspond to the value given for the coefficient  $\beta$ , i.e. 3% of volume variation at the maximum conversion. The final value of volume variation is therefore directly related to the reached conversion value at the end. The figure 9, illustrate the dependency of heat capacity upon temperature and chemical conversion.

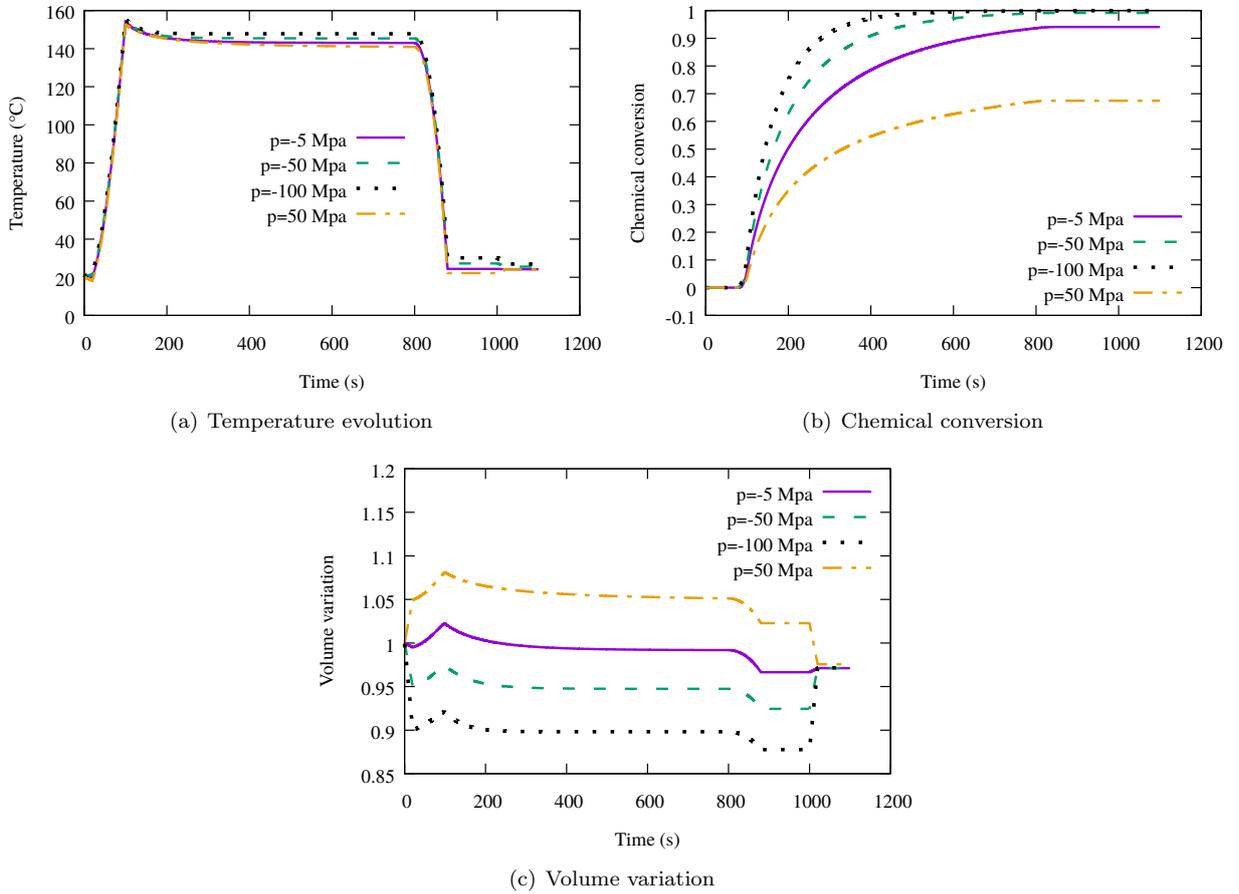


Figure 7: Results of a virtual material processing test under various hydrostatic pressure.

#### 4.4. Example 4: adiabatic case with cyclic shearing and heating, application to chemo-thermal aging upon thermo-mechanical loadings

In this example, it is considered the case of an homogeneous sinusoidal shear test with an initial volumetric heating (as previously with an imposed value of  $\rho_0 r$ ). No heat exchange is considered therefore the solution

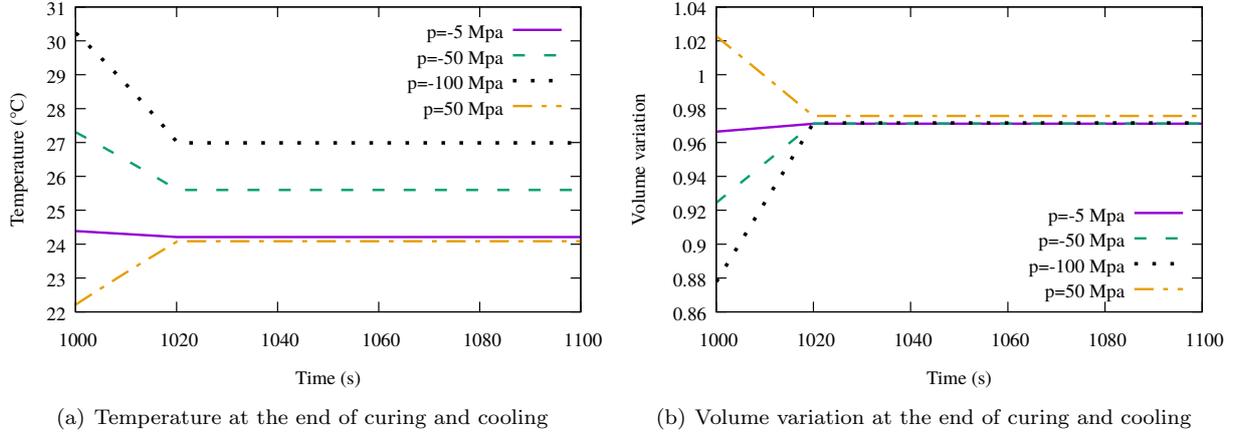


Figure 8: Results of a virtual material processing test under various hydrostatic pressure: zoom at the end of curing.

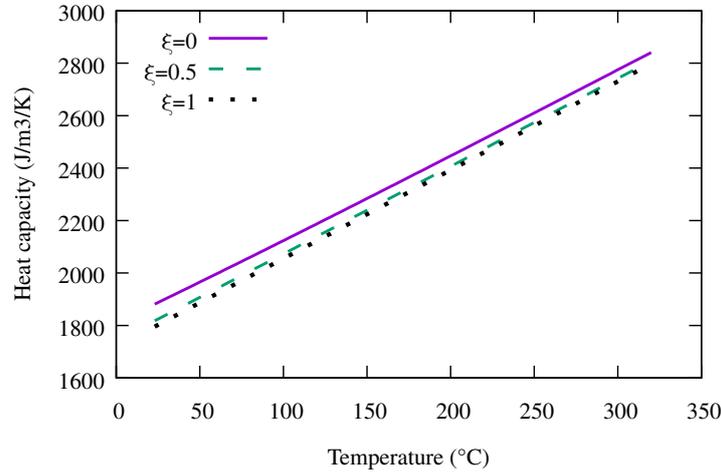


Figure 9: Total heat capacity for  $p = 0$ .

is assumed to be homogeneous. The total deformation gradient is defined from eq (53) and the viscoelastic Cauchy Green tensor is defined from eq (54). The thermal dilatation and the chemical shrinkage are taken into account, the imposed deformation gradient leads to  $J = 1$  and therefore  $J_m$  is explicitly defined as a function of  $\xi$  and  $\Theta$ :

$$J_m = J_\xi^{-1} J_\Theta^{-1} = (1 + \beta g(\xi))^{-1} (1 + \alpha(\Theta - \Theta_0))^{-1} \quad (66)$$

In this case hydrostatic pressure is defined by:

$$p = K_v (J_\xi^{-1} J_\Theta^{-1} - 1) J_\xi^{-1} J_\Theta^{-1} \quad (67)$$

As for the previous example, it is imposed in the first 30 mechanical cycles a volumetric heating to initiate chemical reaction (initial condition of  $\Theta_0 = 20C$  is assumed). The volumetric heating is defined by:

$$\rho_0 r(t) = \begin{cases} 4.2e^6 \times (t/30) J/m^3 & t < 30 \\ 0 & t \geq 30 \end{cases} \quad (68)$$

This idealized example is viewed as a very simplified simulation of thermo-chemical aging of a polymer material. These phenomena are distinct from the previous virtual curing processing however it is assumed

that couplings upon each physics can be represented by the same model. As we do not intend to simulate a real material but only to qualitatively represent observed phenomena, the material parameters are kept identical than previous examples.

In the particular case of simple shear, the shear stress is explicitly given from the constitute equation, it is obtained the following set of equations:

$$\boldsymbol{\sigma}_{12} = 2\gamma(t)(C_{10}(\Theta, \xi) + C_{01}) + 2G(\Theta, \xi)B_{e12}(t) \quad (69)$$

$$\dot{\bar{\mathbf{B}}}_e = \mathbf{L} \cdot \bar{\mathbf{B}}_e + \bar{\mathbf{B}}_e \cdot \mathbf{L}^T - \frac{1}{\tau(\Theta, \xi)} \bar{\mathbf{B}}_e^D \cdot \bar{\mathbf{B}}_e \quad (70)$$

$$\dot{\Theta} = \frac{J}{\rho_0 C(\Theta, \xi, \bar{\mathbf{B}}_e)} (\phi_m(\Theta, \xi, \bar{\mathbf{B}}_e) + \phi_\xi(\Theta, \xi, \bar{\mathbf{B}}_e) + l_m(\Theta, \xi, \bar{\mathbf{B}}_e) + l_c(\Theta, \xi, \bar{\mathbf{B}}_e) + J^{-1} \rho_0 r) \quad (71)$$

$$\dot{\xi} = \frac{A}{J} \exp \frac{-E_a}{R\Theta} \left\langle C_2 \Theta_i \log \left( \frac{\Theta}{\Theta_i} \right) (1 - \xi)^m - \frac{\partial C_{10}}{\partial \xi} \gamma(t)^2 - \frac{\partial G}{\partial \xi} (\text{tr}(\bar{\mathbf{B}}_e) - 3) - \beta \frac{K_v}{2} \frac{\partial g}{\partial \xi} J_\xi^{-1} (J_\xi^{-1} J_\Theta^{-1} - 1)^2 \right\rangle \quad (72)$$

$$\xi(0) = 0, \Theta(0) = \Theta_0, \bar{\mathbf{B}}_e(0) = \mathbf{1} \quad (73)$$

For this example, the mechanical evolution problem has the smaller time scale and it is adopted a staged coupling strategy to save computing time and memory. It is assumed that  $\Theta$  and  $\xi$  does not evolve much during a mechanical period ( $T = 1s$ ). Therefore  $\Theta$  and  $\xi$  are considered as functions of the number of mechanical cycles  $N$ . It is defined the following quantity:

$$\Theta(N) = \Theta_N = \frac{1}{T} \int_{\text{cycle}} \Theta(t) dt \quad \xi(N) = \xi_N = \frac{1}{T} \int_{\text{cycle}} \xi(t) dt \quad (74)$$

The system of equations (69) to (73) is replaced by:

$$\begin{cases} \boldsymbol{\sigma}_{12}(t) = 2\gamma(t)(C_{10}(\Theta_N, \xi_N) + C_{01}) + 2G(\Theta_N, \xi_N)B_{e12}(t) \\ \dot{\bar{\mathbf{B}}}_e(t) = \mathbf{L}(t) \cdot \bar{\mathbf{B}}_e(t) + \bar{\mathbf{B}}_e(t) \cdot \mathbf{L}(t)^T - \frac{1}{\tau(\Theta_N, \xi_N)} \bar{\mathbf{B}}_e(t)^D \cdot \bar{\mathbf{B}}_e(t) \\ \bar{\mathbf{B}}_e(0) = \mathbf{1} \end{cases} \quad (75)$$

$$\begin{cases} \frac{\delta \Theta_N}{\delta \mathbf{N}} = \frac{\int_{\text{cycle}} (\phi_m(\Theta_N, \xi_N, \bar{\mathbf{B}}_e) + \phi_\xi(\Theta_N, \xi_N, \bar{\mathbf{B}}_e) + l_m(\Theta_N, \xi_N, \bar{\mathbf{B}}_e) + l_c(\Theta_N, \xi_N, \bar{\mathbf{B}}_e) + \rho_0 J^{-1} r) dt}{\int_{\text{cycle}} J^{-1} \rho_0 C(\Theta_N, \xi_N, \bar{\mathbf{B}}_e(t)) dt} \\ \frac{\delta \xi_N}{\delta \mathbf{N}} = A \exp \frac{-E_a}{R\Theta} \int_{\text{cycle}} J^{-1} \left\langle C_2 \Theta_i \log \left( \frac{\Theta_N}{\Theta_i} \right) (1 - \xi_N)^m - \frac{\partial C_{10}}{\partial \xi} \gamma(t)^2 - \frac{\partial G}{\partial \xi} (\text{tr}(\bar{\mathbf{B}}_e) - 3) \right. \\ \left. - \beta \frac{K_v}{2} \frac{\partial g}{\partial \xi} J_\xi^{-1} (J_\xi^{-1} J_\Theta^{-1} - 1)^2 \right\rangle dt \\ \xi_{N=0} = 0, \Theta_{N=0} = \Theta_0, \end{cases} \quad (76)$$

For a given cycle  $N$ , the following resolution is adopted: eq (75) are integrated with a forward Euler method. Temperature and chemical state are frozen and all the integral quantity needed to compute system (76) are numerically computed with a rectangle rule. System (76) is also integrated with a rectangle rule.

Figures 10 show the results of the numerical simulation up to  $N = 3000$  cycles. As expected, the higher is the mechanical amplitude the higher is the temperature and the faster is the chemical conversion. The chemo-mechanical coupling is controlled by the dependency of mechanical parameter upon chemical conversion and by the ratio of  $A \times C_2$  versus  $\beta \times A$ . For the chosen values of  $C_2$  and  $A$ , it can be seen that a small change of  $\beta$  can lead to strong differences for the chemical conversion. In this example and for the chosen material parameters, it is needed to bring external heating for initiating chemical reactions. The proposed model is not limited to this case and it could be considered the case of chemical reaction activated only by self heating due to mechanical loadings (however more cycles would be necessary).

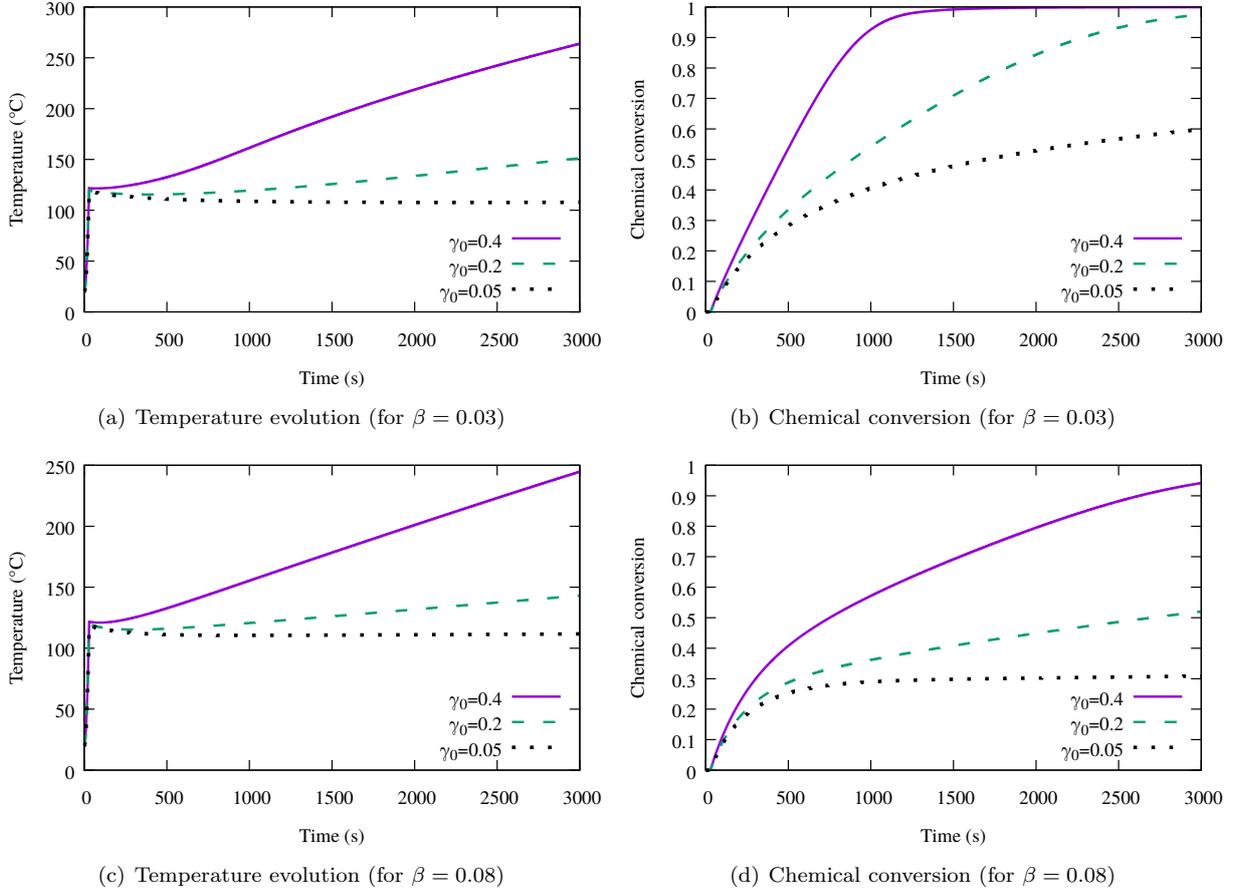


Figure 10: Thermo-Chemical aging for cyclic shearing

## 5. Remarks and conclusion

In this paper, we have developed a rigorous thermodynamical framework for the thermo-chemo-mechanical couplings in soft materials at finite strain. A thermo-viscoelastic model with a kinetic approach for chemistry is proposed. The main originality resides in the definition of the chemical Helmholtz free energy potential and the associated chemical flow rule. The free energy potential takes into account of an initiation temperature under which energy is stored as heat and above which energy is released to initiate chemical conversion. The chemical conversion which is derived from the energy potential naturally takes into account of the hydrostatic pressure. This two points lead to a clear definition of the heat capacity (and the respective influence of temperature and chemistry on it) and to a clear influence of hydrostatic pressure on chemical process. The proposed model is a first step to analyze and simulate complex multiphysics phenomena that take place during processing or aging of soft materials submitted to large strain. In this paper it has been chosen to consider only idealized application without any characterization of a real material. Therefore the chemical (one phenomenological reaction scheme) and the mechanical (zener model) behaviors are chosen as simple as possible to focus on the influence of chemo-mechanical couplings. For a specific application, the question of material parameters identification will certainly become a central one. In the case of non-linear mechanical behavior at finite strain the identification of phenomenological model usually required several experiments to be valid. As example simple DMA experiments are in general not sufficient. Conducting these experiments at controlled (homogeneous in the sample and stable) chemical states seems challenging. Nevertheless, if one consider curing of polymers (or rubbers), chemorheology can give useful informations in the linear regime

(see for instance Joshi and Leonov (2001)). It is therefore needed to develop new testing methods and experimental procedures that could help to investigate the non-linear regime or to impose complex mechanical loadings within a rheometer (for instance a precise control of the hydrostatic pressure, see Mackley and Spitteler (1996)). We believe that numerical simulation with thermo-chemo-mechanical models will greatly help to introduce new experimental technics and will be useful for a better understanding of existing ones. The finite element implementation of the present model requires to pay a careful attention on the variational formulation and on the numerical integrations schemes (for both evolution and conservation equations). The intrinsic times of each physics can be greatly different depending on the application (curing, aging, ...), on the material (polymer, rubbers, ...) and the loading conditions. Depending on these characteristics a monolithic or a staged strategy can be more appropriate. A first attempt has been proposed in Nguyen Van et al. (2012); Eyheramendy et al. (2014) and need further improvements. These numerical developments will permit to take into account of more complex and localized phenomena like heat conduction (thermal gradients) or chemical diffusion.

## References

- André, M., Wriggers, P., 2005. Thermo-mechanical behaviour of rubber materials during vulcanization. *International Journal of Solids and Structures* 42 (1617), 4758 – 4778.  
 URL <http://www.sciencedirect.com/science/article/pii/S0020768305000363>
- Behnke, R., Dal, H., Kaliske, M., 2011. An extended tube model for thermo-viscoelasticity of rubberlike materials: Parameter identification and examples. *PAMM* 11 (1), 353–354.  
 URL <http://dx.doi.org/10.1002/pamm.201110168>
- De Donder, T., 1928. *L'affinité*. M. Lamertin, Bruxelles.
- Dimier, F., Dec. 2003. Reactive systems injection: kinetic and rheological laws determination and modelisation (in french). Theses, École Nationale Supérieure des Mines de Paris.  
 URL <https://pastel.archives-ouvertes.fr/pastel-00001188>
- Eyheramendy, D., Lejeunes, S., Saad, R., Zhang, L., 2014. Advances in symbolic and numerical approaches in computational mechanics. In: Topping, B. H. V., Ivnyi, P. (Eds.), *Computational Methods for Engineering Technology*. Saxe-Coburg Publications, Ch. 3, pp. 61–88.  
 URL <http://dx.doi.org/10.4203/csets.35.3>
- Flory, R. J., 1961. Thermodynamic relations for highly elastic materials. *Transactions of the Faraday Society* 57, 829–838.
- Germain, P., Nguyen, Q., Suquet, P., 1983. Continuum thermodynamics. *Journal of Applied Mechanics* 50, 1010–1020.  
 URL <http://dx.doi.org/10.1115/1.3167184>
- Gigliotti, M., Grandidier, J.-C., 2010. Chemo-mechanics couplings in polymer matrix materials exposed to thermo-oxidative environments. *Comptes Rendus Mecanique* 338 (3), 164 – 175.  
 URL <http://www.sciencedirect.com/science/article/pii/S1631072110000240>
- Gigliotti, M., Grandidier, J.-C., Lafarie-Frenot, M. C., 2011. Assessment of chemo-mechanical couplings in polymer matrix materials exposed to thermo-oxidative environments at high temperatures and under tensile loadings. *Mechanics of Materials* 43 (8), 431 – 443.  
 URL <http://www.sciencedirect.com/science/article/pii/S016766361100069X>
- Halphen, B., Nguyen, Q., 1975. On generalized standard materials. *J. Mech.* 14, 39–63.
- Holzapfel, G., Simo, J., 1996. Entropy elasticity of isotropic rubber-like solids at finite strains. *Computer Methods in Applied Mechanics and Engineering* 132 (12), 17 – 44.  
 URL <http://www.sciencedirect.com/science/article/pii/0045782596010018>
- Joshi, P. G., Leonov, A. I., 2001. Modeling of steady and time-dependent responses in filled, uncured, and crosslinked rubbers. *Rheologica Acta* 40 (4), 350–365.  
 URL <http://dx.doi.org/10.1007/s003970000157>
- Kannan, K., Rajagopal, K., 2011. A thermodynamical framework for chemically reacting systems. *Zeitschrift für Angewandte Mathematik und Physik (ZAMP)* 62, 331–363, 10.1007/s00033-010-0104-1.  
 URL <http://dx.doi.org/10.1007/s00033-010-0104-1>
- Likozar, B., Krajnc, M., 2011. Cross-linking of polymers: Kinetics and transport phenomena. *Industrial & Engineering Chemistry Research* 50 (3), 1558–1570.  
 URL <http://dx.doi.org/10.1021/ie1015415>
- Lion, A., Höfer, P., 2007. On the phenomenological representation of curing phenomena in continuum mechanics. *Arch. Mech.* 59 (1), 59–89.
- Mackley, M., Spitteler, P., 1996. Experimental observations on the pressure-dependent polymer melt rheology of linear low density polyethylene, using a multi-pass rheometer. *Rheologica Acta* 35 (2), 202–209.  
 URL <http://dx.doi.org/10.1007/BF00396047>
- Mahnken, R., 2013. Thermodynamic consistent modeling of polymer curing coupled to viscoelasticity at large strains. *International Journal of Solids and Structures* 50 (13), 2003 – 2021.  
 URL <http://www.sciencedirect.com/science/article/pii/S0020768313000486>

- Nguyen Van, T., Lejeunes, S., Eyheramendy, D., Boukamel, A., 2012. A finite strain thermo-chemo-mechanical coupled model for filled rubber. In: Topping, B. H. V. (Ed.), Proceedings of the Eighth International Conference on Engineering Computational Technology. Civil-Comp Press, Stirlingshire, UK.  
URL <http://dx.doi.org/10.4203/ccp.100.18>
- Onsager, L., 1931. Reciprocal Relations in Irreversible Processes. I. *Physical Review* 37, 405–426.
- Prigogine, I., 1968. Introduction to thermodynamics of irreversible processes. No. third edition. Interscience Publishers.
- Prime, R. B., 1973. Differential scanning calorimetry of the epoxy cure reaction. *Polymer Engineering & Science* 13 (5), 365–371.  
URL <http://dx.doi.org/10.1002/pen.760130508>
- Reese, S., Govindjee, S., 1997. Theoretical and numerical aspects in the thermo-viscoelastic material behaviour of rubber-like polymers. *Mechanics of Time-Dependent Materials* 1, 357–396.  
URL <http://dx.doi.org/10.1023/A:1009795431265>
- Wolfram Research, I., 2014. Mathematica.