

A Finite Strain Thermo-Chemo-Mechanical Coupled Model for Filled Rubber

T.A. Nguyen Van¹, S. Lejeunes¹, D. Eyheramendy² and A. Boukamel³

¹Laboratoire de Mécanique et d'Acoustique, Centre National de la Recherche Scientifique, Aix-Marseille Université, Marseille, France

²Ecole Centrale de Marseille, Laboratoire de Mécanique et d'Acoustique Centre National de la Recherche Scientifique, Marseille, France

³Ecole Hassania des Travaux des Publics, Casablanca, Morocco

Abstract

Rubber parts are strongly sensitive to thermal effects and to the state of cure of the material which can evolve during utilisation. We propose a finite strain thermo-chemo-mechanical model to represent the phenomena related to this coupling. This model is based on the thermodynamics of irreversible processes and on the multiplicative decomposition of the deformation gradient into a mechanical part, a thermal part and a chemical part. The originality of the present approach lies in the introduction of the mechanical contribution in the crosslinking process. Furthermore, the chosen global numerical approach allows us to treat this strong coupling behaviour in a general and robust manner.

Keywords: multi-physics coupling, thermo-chemo-mechanical behaviour, finite element, object-oriented programming, Java.

1 Introduction

In industrial applications, filled rubber parts are usually submitted to strong mechanical and thermal loadings. The high dependence on temperature of their mechanical properties, and a heat build-up phenomenon due to the dissipative behaviour of the material under dynamic loadings, leads to a strong thermo-mechanical coupling. Some material and numerical models of the thermo-mechanical behaviour of rubber can be found in [1-4] and references therein. These models are mainly based either on phenomenological approaches at a macro level [1,3,4] or on micro-mechanical motivations [2]. Some authors have provided validation of these models based on thermo-mechanical experiments, see [1,3].

Furthermore, the properties are strongly dependent on the state of cure of the material. This state of cure is directly linked to the crosslinks density which characterizes the chemical bonds between the macro-molecules chains. These

crosslinks are formed during the vulcanization process. There are several chemical reactions that occur in this process (see [5-7] and references therein). In the literature, one can find two kinds of approaches for describing the vulcanization process: a phenomenological one or a mechanistic one.

In practice, the material is generally not fully crosslinked in order to optimize its properties. Moreover, the distribution of crosslinks in rubber parts can be heterogeneous (see [8]). Thus, the curing of the material may continue after processing (during utilization). This phenomenon can be activated thanks to heat aging or chemical aging but it can also be activated together by mechanical solicitations and by heat build-up process. Therefore, it is important to take into account this chemical phenomenon in the thermo-mechanical coupling. This topic has a growing interest in the literature [11-17] with different materials, e.g.: alloy, concrete, thermoset polymer, epoxy resin and rubber. A thermo mechanical behaviour of rubber material in small deformations during vulcanization process was firstly presented in [11]. The state of cure of this material is described by an internal variable. Finite strain thermo-chemo-mechanical models have been proposed for thermoset and resin e.g. in [15, 17]. The historical dependency on temperature and on curing of the material parameters is considered by an integral approach. In [16], a thermodynamic framework for the response of viscoelastic materials that are undergoing chemical reactions is proposed and takes into account stoichiometry. The authors have proposed to formulate the second law of thermodynamics from Gibbs' potential, which is the natural way to study problems involving chemical reactions. The stoichiometric coefficients of reaction are directly taken into account through a mechanistic approach. An example of sulfur vulcanization process of rubber is presented to validate this theory. However, in the literature, the mechanical contribution to chemical processes has not been fully considered. For example, it is shown experimentally in [18,19] that the hydrostatic pressure could activate the vulcanization process without vulcanization agents.

In this contribution, we propose a finite strain thermo-chemo-mechanical model based on the thermodynamics of irreversible processes and on the introduction of internal variables. We assume that the volume variation is due to three contributions: a mechanical one, a thermal expansion one, a chemical shrinkage one. Furthermore, the mechanical deformation is restricted to nearly incompressible case. For this model the mechanical behaviour is based on a hyper visco-plastic law. For the chemical part, an idealized vulcanization evolution law that takes into account hydrostatic effects is considered. We propose a monolithic resolution scheme based on a mixed variational formulation adapted to the resolution of the mechanical, thermal and chemical balance equations within the weak compressibility constraint in a fully coupled way. This formulation is implemented into the F.E code FemJava [19].

In Section 2, the global thermodynamical framework is introduced. The thermo-chemo-mechanical coupled model is presented in Section 3. The variational formulation of this model and the implementation of this formulation in the oriented-object code FEMJava is presented in Section 4. In Section 5, we propose some numerical illustrations for the proposed thermo-chemo-mechanical strongly coupled.

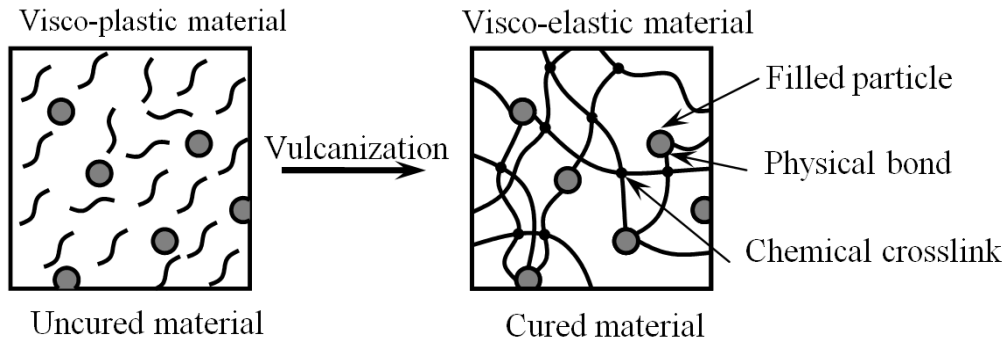


Figure 1: Molecular schematization of vulcanization process (from [11]).

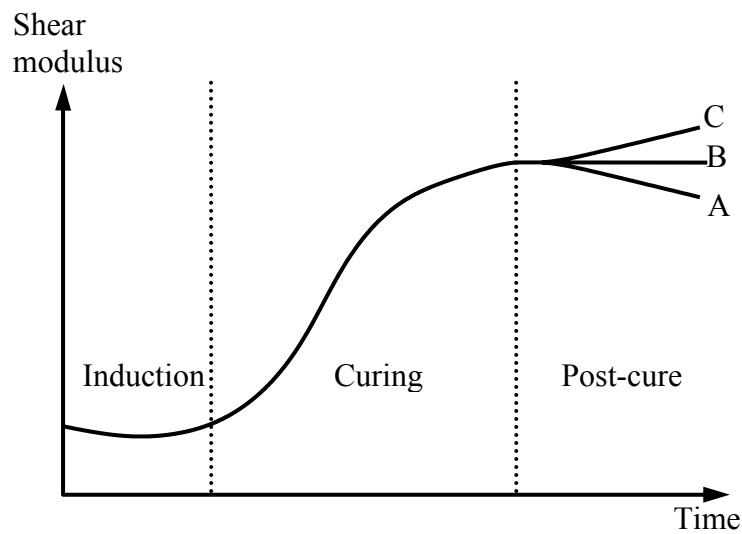


Figure 2: A typical rheometer cure curve obtained from an Oscillating Disk Rheometer for accelerated sulfur vulcanization. Curve A: Cure to maximum torque with reversion. Curve B: Cure to equilibrium torque. Curve C: Cure with no equilibrium or maximum torque (from [5])

2 Thermodynamical framework

In this paper, we use the phenomenological approach based on the thermodynamics of irreversible processes and the introduction of internal variable to describe history effects and chemical evolution. In this approach, the deformation gradient \mathbf{F} and the absolute temperature θ are the state variables.

2.1 Chemical internal variable

Natural or synthetic rubbers are composed of long polymer chains and fillers. In the uncured state, polymer chains and fillers are weakly connected between each others, and the material behaves like a fluid (Figure 1). The vulcanization process creates strong physical bonds between the chains (crosslinks) and the material behaves as a

solid. The chemical process of vulcanization is complex and embeds several reactions. More details of this process can be found e.g. [5-8]. The vulcanization process is composed of three phases: induction phase, curing phase and post-curing phase. In Figure 2, these three phases can be seen from the evolution of shear modulus in regard to the curing time. The vulcanization process can be schematized by the following system of equations:

$$\begin{aligned}
\nu_{11}S_1 + \nu_{12}S_2 + \cdots + \nu_{1n}S_n + \nu_{1Vu}S_{Vu} &= 0 \\
\nu_{21}S_1 + \nu_{22}S_2 + \cdots + \nu_{2n}S_n + \nu_{2Vu}S_{Vu} &= 0 \\
\vdots & \\
\nu_{m1}S_1 + \nu_{m2}S_2 + \cdots + \nu_{mn}S_n + \nu_{mVu}S_{Vu} &= 0
\end{aligned} \tag{1}$$

where S_i represents the i -th chemical species, S_{Vu} the vulcanizate product, the ν_{ij} are stoichiometric coefficients.

The equation of mass conservation for reaction (1) can be written as follows:

$$m_{s_1} + m_{s_2} + \cdots + m_{s_n} + m_{s_{Vu}} = m = \text{const} \tag{2}$$

We define the state of cure, ξ as follows:

$$\xi = \frac{m_{s_{Vu}}}{m}; \quad 0 \leq \xi \leq 1 \tag{3}$$

where $\xi = 0$ corresponds to uncured rubber and $\xi = 1$ corresponds to totally cured rubber. In the following we consider ξ as an internal variable.

2.2 Kinematics

As in [17,21], it is assumed that the deformation gradient is split into three parts: a mechanical part, a thermal part and a chemical part.

$$\mathbf{F} = \mathbf{F}_M \mathbf{F}_C \mathbf{F}_T \tag{4}$$

The choice of the decomposition is arbitrary as the thermal and chemical deformations can not be dissociated. However, we consider only volume variation for thermal and chemical deformations. This volume variation can be observed during the vulcanization process, see [6,7]. Therefore, we assume the following:

$$\begin{aligned}
\mathbf{F}_T &= \left(1 + \alpha(\theta - \theta_{ref})\right)^{\frac{1}{3}} \mathbf{1} \\
\mathbf{F}_C &= \left(1 + \beta g(\xi, \xi_{ref})\right)^{\frac{1}{3}} \mathbf{1}
\end{aligned} \tag{5}$$

where α, β are the coefficients of thermal expansion, chemical shrinkage respectively; θ, θ_{ref} are the absolute temperature at the current, reference state, ξ, ξ_{ref} are the degree of cure at the current, reference state respectively; $g(\xi, \xi_{ref})$ is the shrinkage function depending on the degree of cure; $\mathbf{1}$ is the identity tensor. We suppose the existence of a natural state which is identical to reference configuration, $\mathbf{F}_M = \mathbf{1}, \theta = \theta_{ref}, \xi = \xi_{ref}$ which is stress-free configuration.

The mechanical transformation is then split into volumetric one and deviatoric one in order to take into account the nearly incompressible mechanical constraint:

$$\mathbf{F}_M = \bar{\mathbf{F}}_M J_M^{1/3} \mathbf{1} \quad (6)$$

where $\bar{\mathbf{F}}_M$ and J_M are respectively the isochoric part of the mechanical deformation gradient and the mechanical volume variation. Finally, the decomposition of the transformation can be written as:

$$\mathbf{F} = \bar{\mathbf{F}}_M (J_M J_T J_C)^{1/3} \text{ and } \bar{\mathbf{F}}_M = \bar{\mathbf{F}} \quad (7)$$

where $\bar{\mathbf{F}}$ is the isochoric part of the total deformation gradient.

The proposed model will not take into account a deviatoric stress due to the chemical process. In [15], an isochoric part for chemical deformation gradient is considered. To take into account the history effects of mechanical transformation, we consider the following classical decomposition into elastic part $\bar{\mathbf{F}}_e$ and inelastic part $\bar{\mathbf{F}}_i$:

$$\bar{\mathbf{F}}_M = \bar{\mathbf{F}}_e \bar{\mathbf{F}}_i \quad (8)$$

2.3 Thermodynamic principles and hypothesis

We consider only isotropic behaviour and the specific free energy is assumed to be a function of state and internal variables:

$$\Psi = \Psi(\bar{\mathbf{B}}, \bar{\mathbf{B}}_e, J, \theta, \xi) \quad (9)$$

where $\bar{\mathbf{B}}, \bar{\mathbf{B}}_e$ are the left Cauchy-Green deformations associated to $\bar{\mathbf{F}}, \bar{\mathbf{F}}_e$.

In the context of thermodynamics of irreversible processes, the constitutive equations must fulfill the Clausius-Duhem inequality, which takes the following form in the Eulerian configuration:

$$\Phi = \boldsymbol{\sigma} : \mathbf{D} - \rho_o J^{-1} \dot{\Psi} - \rho_o J^{-1} s \dot{\theta} - \frac{1}{\theta} q \cdot \text{grad} \theta \geq 0 \quad (10)$$

where $\boldsymbol{\sigma}$ is the Cauchy stress, \mathbf{D} is the Eulerian rate of deformation, ρ_o is the volumetric mass in reference configuration, s is the entropy, q is the heat flux, Φ is the internal dissipation.

The time variation of the specific energy is given as follows:

$$\dot{\Psi} = \frac{\partial \Psi}{\partial \bar{\mathbf{B}}} : \dot{\bar{\mathbf{B}}} + \frac{\partial \Psi}{\partial \bar{\mathbf{B}}_e} : \dot{\bar{\mathbf{B}}_e} + \frac{\partial \Psi}{\partial J} : \dot{J} + \frac{\partial \Psi}{\partial \theta} : \dot{\theta} + \frac{\partial \Psi}{\partial \xi} : \dot{\xi} \quad (11)$$

where

$$\begin{aligned} \dot{\bar{\mathbf{B}}} &= \mathbf{L} \bar{\mathbf{B}} + \bar{\mathbf{B}} \mathbf{L}^T - \frac{2}{3} (\mathbf{1} : \mathbf{D}) \bar{\mathbf{B}} \\ \dot{\bar{\mathbf{B}}}_e &= \mathbf{L} \bar{\mathbf{B}}_e + \bar{\mathbf{B}}_e \mathbf{L}^T - 2 \bar{\mathbf{V}}_e \bar{\mathbf{D}}_i^\circ \bar{\mathbf{V}}_e - \frac{2}{3} (\mathbf{1} : \mathbf{D}) \bar{\mathbf{B}}_e \\ \dot{J} &= J (\mathbf{1} : \mathbf{D}) \end{aligned} \quad (12)$$

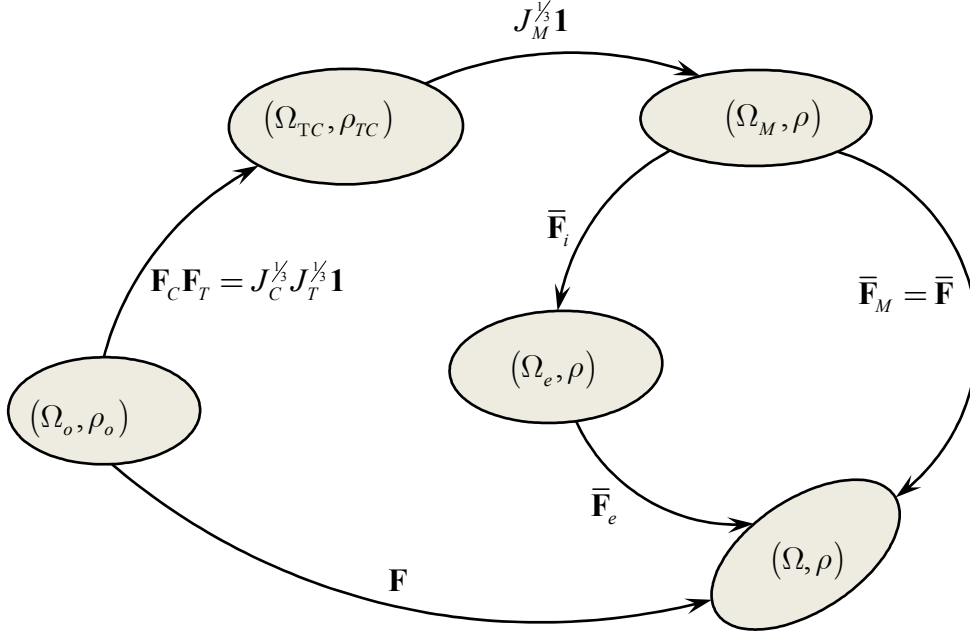


Figure 3: The intermediate configurations of a thermo-chemo-mechanical process

where $\bar{\mathbf{D}}_i^o$ is the objective rate of inelastic deformation, $\bar{\mathbf{D}}_i^o = \mathbf{R}_e \bar{\mathbf{D}}_i \mathbf{R}_e^T$. \mathbf{R}_e is the elastic rotation coming from polar decomposition of elastic deformation gradient. Replacing the equations (12) and (11) in (10), we obtain:

$$\begin{aligned} \Phi = & \left[\boldsymbol{\sigma} - 2\rho_o J^{-1} \left(\bar{\mathbf{B}} \frac{\partial \Psi}{\partial \bar{\mathbf{B}}} + \bar{\mathbf{B}}_e \frac{\partial \Psi}{\partial \bar{\mathbf{B}}_e} \right)^D - \rho_o \frac{\partial \Psi}{\partial J} \mathbf{1} \right] : \mathbf{D} + 2\rho_o J^{-1} \left(\bar{\mathbf{B}}_e \frac{\partial \Psi}{\partial \bar{\mathbf{B}}_e} \right) : \bar{\mathbf{D}}_i^o \\ & - \rho_o J^{-1} \left(s + \frac{\partial \Psi}{\partial \theta} \right) \dot{\theta} - \rho_o J^{-1} \frac{\partial \Psi}{\partial \xi} \dot{\xi} - \frac{1}{\theta} q \cdot \text{grad} \theta \geq 0 \end{aligned} \quad (13)$$

Starting from (13), we make the following hypothesis:

- The entropy definition:

$$s = -\frac{\partial \Psi}{\partial \theta} \quad (14)$$

- The stress definition:

$$\boldsymbol{\sigma} = \left(2\rho_o J^{-1} \bar{\mathbf{B}} \frac{\partial \Psi}{\partial \bar{\mathbf{B}}} + 2\rho_o J^{-1} \bar{\mathbf{B}}_e \frac{\partial \Psi}{\partial \bar{\mathbf{B}}_e} \right)^D + \rho_o \frac{\partial \Psi}{\partial J} \mathbf{1} \quad (15)$$

The remainder of dissipation is composed of three terms:

$$\Phi = \Phi_M + \Phi_T + \Phi_C \geq 0 \quad (16)$$

In order to ensure the non-negativeness of internal dissipation for all admissible processes, we suppose, the positiveness of each dissipation terms independently of the others. Therefore, we must have:

$$\begin{aligned}
\Phi_M &= \left(2\rho_o J^{-1} \bar{\mathbf{B}}_e \frac{\partial \Psi}{\partial \bar{\mathbf{B}}_e} \right)^D : \bar{\mathbf{D}}_i^o \geq 0 \\
\Phi_C &= -\rho_o J^{-1} \frac{\partial \Psi}{\partial \xi} \dot{\xi} \geq 0 \\
\Phi_T &= -\frac{q}{\theta} \text{grad}(\theta) \geq 0
\end{aligned} \tag{17}$$

4 A phenomenological thermo-chemo-mechanical model

The specific free energy is then supposed to split additively into mechanical part, thermal part and chemical part as follows:

$$\Psi(\bar{\mathbf{B}}, \bar{\mathbf{B}}_e, J, \theta, \xi) = \underbrace{\psi_{eq}(\bar{\mathbf{B}}, \theta, \xi) + \psi_{neq}(\bar{\mathbf{B}}_e, \theta, \xi)}_{\text{mechanical part}} + \underbrace{\psi_{vol}(J, \theta, \xi)}_{\text{thermal part}} + \underbrace{\psi_T(\theta) + \psi_C(\theta, \xi)}_{\text{chemical part}} \tag{18}$$

To ensure the positiveness of each dissipation term of equation (17), we introduce a pseudo-potential of dissipation φ^* which is a convex positive function of force variables and we use the normality principle to obtain the force-flux rules. Furthermore, this pseudo-potential of dissipation is decomposed as follows:

$$\varphi^* \left(\sigma, \frac{\text{grad}(\theta)}{\theta}, F_C \right) = \varphi_M^*(\sigma) + \varphi_T^* \left(\frac{\text{grad}(\theta)}{\theta} \right) + \varphi_C^*(F_C) \tag{19}$$

where F_C is the chemical force defined by:

$$F_C = -\rho_o J^{-1} \frac{\partial \psi}{\partial \xi} \tag{20}$$

4.1 Mechanical model

As explained in the introduction, the behaviour of filled rubber is generally viscoplastic in the uncured state and more viscoelastic in the cured state. In this paper, we have chosen a very simple viscoplastic rheological model based on Bingham viscoplastic cell (see Figure 4). For this model, the specific free energy is chosen as follows:

$$\begin{aligned}
\rho_o \psi_{eq}(\bar{\mathbf{B}}, \theta, \xi) &= C_{10}(\theta, \xi) (\bar{I}_1 - 3) + C_{01}(\theta, \xi) (\bar{I}_2 - 3) \\
\rho_o \psi_{neq}(\bar{\mathbf{B}}_e, \theta, \xi) &= C_{e10}(\theta, \xi) (\bar{I}_{1e} - 3) \\
\rho_o \psi_{vol}(J, \theta, \xi) &= \frac{1}{2} K_v(\theta, \xi) (J_M - 1)^2 = \frac{1}{2} K_v(\theta, \xi) (JJ_T^{-1} J_C^{-1} - 1)^2
\end{aligned} \tag{21}$$

The material parameter K_v is the bulk modulus of material and the mechanical volumetric part of free energy is assumed to be only dependent on J_M, K_v (which could be temperature and degree of cure dependent). Therefore, in the case of isothermal and iso-chemical processes, we recover the classical form for the volumetric free energy. We define the elastic domain $\mathbf{E} = \{\boldsymbol{\sigma}_{neq} \mid f(\boldsymbol{\sigma}_{neq}) \leq 0\}$ from the yield function f as in classical $J2$ plastic flow:

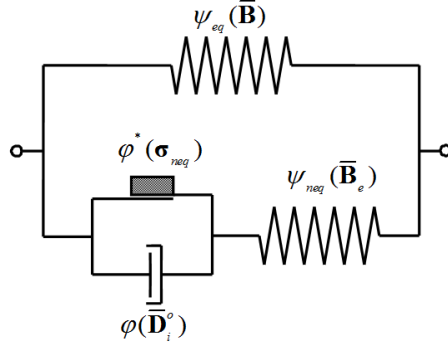


Figure 4: A hyper-viscoplastic model of Bingham

$$f(\boldsymbol{\sigma}_{neq}) = \|\boldsymbol{\sigma}_{neq}\| - \chi(\theta, \xi) \quad (22)$$

where $\|\cdot\|$ stands for the norm operator, $\chi(\theta, \xi)$ is a yield parameter, $\boldsymbol{\sigma}_{neq}$ is the non-equilibrium part of stress. We adopt the following form for the pseudo potential of dissipation:

$$\varphi_M^*(\boldsymbol{\sigma}_{neq}, \theta, \xi) = \frac{1}{2} \frac{\langle f(\boldsymbol{\sigma}_{neq}) \rangle^2}{\eta(\theta, \xi)} \quad (23)$$

where $\eta(\theta, \xi)$ is a viscosity parameter, $\langle \cdot \rangle$ are the Macaulay brackets¹.

Applying the normality principle gives :

$$\mathbf{D}_i^o = \frac{1}{\eta(\theta, \xi)} \frac{\langle f \rangle}{\|\boldsymbol{\sigma}_{neq}\|} \boldsymbol{\sigma}_{neq} \quad (24)$$

Replacing (24) in (12), we obtain the following flow rule:

$$\dot{\bar{\mathbf{B}}}_e = \mathbf{L}\bar{\mathbf{B}}_e + \bar{\mathbf{B}}_e\mathbf{L}^T - \frac{2}{3}(\mathbf{1} : \mathbf{D})\bar{\mathbf{B}}_e - 2 \frac{\langle f \rangle}{\eta(\theta, \xi)} \frac{\boldsymbol{\sigma}_{neq}}{\|\boldsymbol{\sigma}_{neq}\|} \bar{\mathbf{B}}_e \quad (25)$$

The constitutive equations of this model are given by:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{eq} + \boldsymbol{\sigma}_{neq} - p\mathbf{1} \quad (27)$$

$$\boldsymbol{\sigma}_{eq} = \left(2\rho_o J^{-1} \bar{\mathbf{B}} \frac{\partial \psi_{eq}}{\partial \bar{\mathbf{B}}} \right)^D \quad (28)$$

$$\boldsymbol{\sigma}_{neq} = \left(2\rho_o J^{-1} \bar{\mathbf{B}}_e \frac{\partial \psi_{neq}}{\partial \bar{\mathbf{B}}_e} \right)^D \quad (29)$$

$$p = -\rho_o \frac{\partial \psi_{vol}}{\partial J} \quad (30)$$

where p stands for the hydrostatic pressure.

¹ Operator $\langle \cdot \rangle$ is defined by $\langle f \rangle = f$ if $f \geq 0$ and $\langle f \rangle = 0$ if $f < 0$

4.2 Chemical model

In the following, we consider an idealized vulcanization process which is modeled through the introduction of a chemical free energy chosen as follow:

$$\psi_C = \left(A(\theta) \frac{(1-\xi)^{n+1}}{n+1} + A(\theta_{ref})(1-\xi_{ref})^n \xi \right) - \psi_{Cref} \quad (31)$$

where ψ_{Cref} is a constant term such as the chemical free energy is zero in the reference configuration, the temperature dependence of chemical free energy is defined by the Arrhenius law which is given as follows:

$$A(\theta) = A_o e^{\frac{-E_a}{R\theta}} \quad (32)$$

where $R=8.314\text{J/mol/K}$ is the universal gas constant; E_a is the activation energy of chemical reaction; A_o is the pre-exponential factor.

Using equation (20), the chemical force is defined from:

$$F_c = -\rho_o J^{-1} \frac{\partial \psi_C}{\partial \xi} - \rho_o J^{-1} \frac{\partial \psi_{vol}}{\partial \xi} - \rho_o J^{-1} \frac{\partial \psi_{eq}}{\partial \xi} - \rho_o J^{-1} \frac{\partial \psi_{neq}}{\partial \xi} \quad (33)$$

And we have:

$$\begin{aligned} -\rho_o \frac{\partial \psi_C}{\partial \xi} &= \rho_o A(\theta)(1-\xi)^n - \rho_o A(\theta_{ref})(1-\xi_{ref})^n \\ -\rho_o \frac{\partial \psi_{vol}}{\partial \xi} &= -\frac{1}{2} \frac{\partial K_v}{\partial \xi} (JJ_T^{-1} J_C^{-1} - 1)^2 - \beta \frac{\partial g}{\partial \xi} JJ_C^{-1} p \\ -\rho_o \frac{\partial \psi_{eq}}{\partial \xi} &= -\frac{\partial C_{10}}{\partial \xi} (\bar{I}_1 - 3) - \frac{\partial C_{01}}{\partial \xi} (\bar{I}_2 - 3) \\ -\rho_o \frac{\partial \psi_{neq}}{\partial \xi} &= -\frac{\partial C_{e10}}{\partial \xi} (\bar{I}_{1e} - 3) \end{aligned} \quad (34)$$

From this formulation, the mechanical dependency in the chemical force through the hydrostatic pressure and invariants of deformation are obtained. However, in the literature, we can find very few results that show these effects. In [18,19], the effect of hydro static pressure on the vulcanization process is shown. In the future, the influence of mechanical contribution to chemical force needs to be carefully investigated through experiments.

As we do not intend to take into account chemical reversion in this model, we propose the following chemical pseudo-potential of dissipation:

$$\varphi_C^* = \frac{1}{2} h(\theta, \xi) \langle F_c \rangle^2 \quad (35)$$

where $h(\theta, \xi)$ is a chemical parameter. Therefore, the chemical dissipation is zero when the chemical force is negative. The application of the normality principle of force-flux leads to following expression:

$$\dot{\xi} = h(\theta, \xi) \langle F_c \rangle \quad (36)$$

In the case of stress-free, there are only two first terms in chemical force and we recover the curing equation proposed by [5] for vulcanization of rubber.

4.3 Thermal model

For the thermal free energy, we adopt a first term similar to that proposed by [4] and a supplementary term which leads to a linear temperature dependency for heat capacity:

$$\rho_o \psi_T = C_o \left(\theta - \theta_{ref} - \theta \ln \left(\frac{\theta}{\theta_{ref}} \right) \right) - \frac{C_1}{\theta_{ref}} \frac{(\theta - \theta_{ref})^2}{2} \quad (37)$$

For thermal pseudo-potential of dissipation, the following form is proposed:

$$\varphi_T^* = \frac{k(\theta, \xi)}{2\theta} \text{grad}(\theta) \text{grad}(\theta) \quad (38)$$

where $k(\theta, \xi)$ is thermal conductivity coefficient. This choice leads to the classical Fourier law of heat conduction:

$$q = -k(\theta, \xi) \cdot \text{grad}(\theta) \quad (39)$$

4.4 Balance equations

Since we do not consider material exchange in the idealized vulcanization process, the balance of mass for the system is as follows:

$$\begin{aligned} \dot{\rho} + \text{div}(\rho v) &= 0 \\ \text{or } \rho &= \rho_o J^{-1} \end{aligned} \quad (40)$$

In the quasi-static case, the local mechanical equilibrium can be written as, in the Eulerian configuration:

$$\begin{aligned} \text{div}(\boldsymbol{\sigma}) + \rho f_{vol} &= 0 \quad \text{in } \Omega \\ \boldsymbol{\sigma} n &= F_{surf} \quad \text{on } \partial\Omega_F \\ u &= u_o \quad \text{on } \partial\Omega_u \end{aligned} \quad (41)$$

where f_{vol} is the volumetric force in current configuration, Ω is the current domain, n is the normal on the current boundary of imposed forces $\partial\Omega_F$, F_{surf} are the current imposed forces on this boundary, u_o is the imposed kinematic field on the boundary $\partial\Omega_u$.

Using the variation of internal energy (from the first thermodynamical principle), the definition of entropy (14) and the variation of free energy (11), one obtain the following local form of heat balance in Eulerian configuration:

$$\begin{aligned} \rho_o J^{-1} C \dot{\theta} &= \Phi_{\text{int}} - \theta \frac{\partial \boldsymbol{\sigma}_{neg}}{\partial \theta} : \bar{\mathbf{D}}_i^o + \theta (\mathbf{1}_M : \mathbf{D}) + \theta (l_C \cdot \dot{\xi}) \\ &\quad - \text{div}(q) + \rho_o J^{-1} r \end{aligned} \quad \text{in } \Omega$$

$$\begin{aligned}
qn &= q_o && \text{on } \partial\Omega_q && (42) \\
\theta &= \theta_o && \text{on } \partial\Omega_\theta \\
\theta(t=0) &= \theta_{\text{initial}} && \text{in } \Omega
\end{aligned}$$

where C is the heat capacity C at constant deformation:

$$\begin{aligned}
\rho_o C &= -\theta \frac{\partial^2 \rho_o \psi}{\partial \theta^2} = C_1 \frac{\theta}{T_o} + C_0 + C_M + C_C && (43) \\
C_C &= -\rho_o \theta^{-2} \left[A(\theta) \frac{E_a}{R} \left(\frac{E_a}{R} \theta^{-1} - 2 \right) \right] \frac{(1-\xi)^{n+1}}{n+1} \\
C_M &= -\theta \frac{\partial^2 \rho_o \psi_{eq}}{\partial \theta^2} - \theta \frac{\partial^2 \rho_o \psi_{neq}}{\partial \theta^2} - \theta \frac{\partial^2 \rho_o \psi_{vol}}{\partial \theta^2}
\end{aligned}$$

Therefore, the heat capacity is a nonlinear function of the temperature, the degree of cure and the deformation.

And Φ_{int} is the intrinsic dissipation:

$$\Phi_{\text{int}} = \Phi_M + \Phi_C \quad (44)$$

And r is the radiant heat term, \mathbf{l}_M, l_C are the mechanical and chemical latent heat terms:

$$\mathbf{l}_M = \rho_o J^{-1} \left[2\bar{\mathbf{B}} \frac{\partial^2 \psi}{\partial \theta \partial \bar{\mathbf{B}}} + 2\bar{\mathbf{B}}_e \frac{\partial^2 \psi}{\partial \theta \partial \bar{\mathbf{B}}_e} \right]^D - \frac{\partial p}{\partial \theta} \mathbf{1} \quad (45)$$

$$\begin{aligned}
l_C &= \rho_o J^{-1} \frac{\partial^2 \psi}{\partial \theta \partial \xi} \\
\frac{\partial p}{\partial \theta} &= -\rho_o \frac{\partial^2 \psi}{\partial \theta \partial J} && (46)
\end{aligned}$$

In heat balance equation, the variation of temperature is due to intrinsic dissipation term, thermal mechanical coupling terms (usually called as latent heat), thermo-chemo coupling terms, conduction heat term and radiant heat term.

5 Variational formulation and numerical implementation

5.1 Variational formulation

In the aim of reducing the effort for implementing this model and as we also have previously developed model in finite element code, we choose to rewrite the mechanical balance equation in mixed configuration. Starting from the definition of the first Piola-Kirchhoff stress $\mathbf{\Pi} = J\boldsymbol{\sigma}\mathbf{F}^{-T}$, the local equation (41) becomes:

$$\text{DIV}(\mathbf{\Pi}) + \rho_o f_{vol} = 0 \quad \text{in } \Omega_o \quad (47)$$

$$\mathbf{\Pi}N = F_{surf} \quad \text{on } \partial\Omega_{oF}$$

$$u = u_o \quad \text{on } \partial\Omega_{ou}$$

where DIV stands for Lagrangian divergence, N is the normal of undeformed boundary $\partial\Omega_{oF}$. We can do the same for the heat balance equation, and it is obtained :

$$\begin{aligned}
\rho_o J^{-1} C \dot{\theta} &= \Phi_{\text{int}} - \theta \frac{\partial \boldsymbol{\sigma}_{neq}}{\partial \theta} : \bar{\mathbf{D}}_i^o + \theta (\mathbf{1}_M : \mathbf{D}) + \theta (l_c \cdot \dot{\xi}) \\
&\quad - \text{DIV}(Q) + \rho_o J^{-1} r && \text{in } \Omega \\
QN &= Q_o && \text{on } \partial\Omega_q \\
\theta &= \theta_o && \text{on } \partial\Omega_\theta \\
\theta(t=0) &= \theta_{\text{initial}} && \text{in } \Omega
\end{aligned} \tag{48}$$

where $Q = \mathbf{JF}^{-1}q$ and $Q_o = q_o J \sqrt{N \mathbf{F}^{-1} \mathbf{F}^{-T} N}$

To take account of the weak compressibility constraint, we consider the hydrostatic pressure p as a supplementary unknown in the balance equations. Therefore, we also introduce another supplementary unknown dp_θ which stands for the variation of p upon temperature. By using the divergence theorem, integration by parts, and the heat Fourier law (39), we can obtain the following weak form of local equations (26), (30), (36), (47), (48):

$$\begin{aligned}
&\text{Find } (u, \theta, \xi, p, dp_\theta) \quad \forall (\delta u, \delta \theta, \delta \xi, \delta p, \delta dp_\theta) \\
&\int_{\Omega_o} \left(\boldsymbol{\Pi}^{iso}(u) - p \mathbf{JF}^{-T} \right) : \nabla \delta u d\Omega - \int_{\Omega_o} f_{vol} \delta u d\Omega - \int_{\partial\Omega_{oF}} F_{surf} \delta u dS = 0 \tag{49}
\end{aligned}$$

$$\begin{aligned}
&\int_{\Omega_o} \left(\rho_o C \dot{\theta} - \rho_o r - J \Phi_{\text{int}} - J \theta (\mathbf{1}_M : \mathbf{D}) + J \theta \frac{\partial \boldsymbol{\sigma}_{neq}}{\partial \theta} : \bar{\mathbf{D}}_i^o - \theta l_c \dot{\xi} \right) \delta \theta d\Omega \\
&\quad + \int_{\Omega_o} \mathbf{K}_L \nabla_x \theta \cdot \nabla_x \delta \theta d\Omega + \int_{\partial\Omega_{oQ}} Q_o \delta \theta dS = 0 \tag{50}
\end{aligned}$$

$$\int_{\Omega_o} J \left(\dot{\xi} - h \langle F_c(u, \theta, \xi, p) \rangle \right) \delta \xi d\Omega = 0 \tag{51}$$

$$\int_{\Omega_o} \left(-p/K_v - (JJ_t^{-1}J_c^{-1} - 1) J_t^{-1} J_c^{-1} \right) \delta p d\Omega = 0 \tag{52}$$

$$\int_{\Omega_o} \left(-\frac{dp_\theta}{K_v} - \alpha J_t^{-2} J_c^{-1} (1 - 2JJ_t^{-1}J_c^{-1}) \right) \delta dp_\theta d\Omega = 0 \tag{53}$$

where $Q = -\mathbf{K}_L \nabla_x(\theta)$ with $K_L = \mathbf{JF}^{-1}k(\theta, \xi) \mathbf{F}^{-T}$. The isochoric part of the first Piola-Kirchhoff stress is $\boldsymbol{\Pi}^{iso} = J(\boldsymbol{\sigma}_{eq} + \boldsymbol{\sigma}_{neq}) \mathbf{F}^{-T}$.

This variational formulation leads to the discretization of five fields. To our knowledge, the introduction of the new field dp_θ has not been proposed yet in the literature. The idea is to release the local condition on temperature variation of hydrostatic pressure. This condition is a constraint for the unknown field p . For

more precisions on the variational formulation and the finite element implementation in the context of mixed formulations for incompressible media submitted to large strain, we refer to the work of [23] and references therein.

5.2 Numerical implementation

We adopt a classical finite element discretization scheme with a quadratic interpolation for u, θ, ξ . For p, dp_θ , we adopt a local elemental linear interpolation, discontinuous between elements. The nonlinear time dependent system of equations is resolved by the linearization of a Backward-Euler Scheme and the classical Newton-Raphson approach is used. The final global system can be written as:

$$\underbrace{\begin{bmatrix} K_{uu} & K_{up} & K_{ut} & K_{uc} & 0 \\ K_{pu} & K_{pp} & K_{p\theta} & K_{p\xi} & 0 \\ \tilde{K}_{\theta u} & 0 & \tilde{K}_{\theta\theta} & \tilde{K}_{\theta\xi} & \tilde{K}_{\theta dp_\theta} \\ \tilde{K}_{\xi u} & \tilde{K}_{\xi p} & \tilde{K}_{\xi\theta} & \tilde{K}_{\xi\xi} & 0 \\ K_{dp_\theta u}^e & 0 & K_{dp_\theta\theta}^e & K_{dp_\theta\xi}^e & K_{dp_\theta dp_\theta}^e \end{bmatrix}}_{\tilde{K}} \begin{bmatrix} \Delta u \\ \Delta p \\ \Delta \theta \\ \Delta \xi \\ \Delta dp_\theta \end{bmatrix} = \underbrace{\begin{bmatrix} -R_u \\ -R_p \\ -\tilde{R}_\theta \\ -\tilde{R}_\xi \\ -R_{dp_\theta} \end{bmatrix}}_{\tilde{R}} \quad (54)$$

where \tilde{K} is the tangent matrix and \tilde{R} is the residue, defined by the linearization of the Backward Euler scheme. The discontinuity of the fields p, dp_θ allows us to proceed to a static condensation of these fields inside element.

$$\begin{aligned} \Delta p^e &= \left(K_{pp}^e\right)^{-1} \left(-R_p - K_{pu}^e \Delta u - K_{p\theta}^e \Delta \theta - K_{p\xi}^e \Delta \xi\right) \\ \Delta dp_\theta^e &= \left(K_{dp_\theta dp_\theta}^e\right)^{-1} \left(-R_{dp_\theta} - K_{dp_\theta u}^e \Delta u - K_{dp_\theta\theta}^e \Delta \theta - K_{dp_\theta\xi}^e \Delta \xi\right) \end{aligned} \quad (55)$$

The assembled global system becomes:

$$\begin{bmatrix} K'_{uu} & K'_{u\theta} & K'_{u\xi} \\ K'_{\theta u} & K'_{\theta\theta} & K'_{\theta\xi} \\ K'_{\xi u} & K'_{\xi\theta} & K'_{\xi\xi} \end{bmatrix} \begin{bmatrix} \Delta u \\ \Delta \theta \\ \Delta \xi \end{bmatrix} = \begin{bmatrix} R'_u \\ R'_\theta \\ R'_\xi \end{bmatrix} \quad (56)$$

where K' is the condensed tangent matrix and R' is the condensed residue.

The local mechanical flow rule (25) is integrated through a Backward Euler scheme (see [23] for more details).

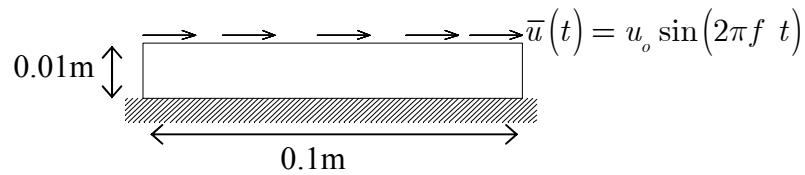


Figure 5: Description of the simple shear test problem.

This model has been implemented in the object-oriented finite element code FemJava. This code is written in Java and is suitable for easily developing strongly coupled multi-physic model, including constitutive laws (see [19]). We simply add two classes corresponding to both the thermo-chemo-mechanical variational model and the constitutive law.

6 Numerical example

We consider a classical simple shear test problem under sinusoidal cyclic imposed displacement (see Figure 5). In the following, we consider simple constant and linear material parameters dependence:

$$\begin{aligned}
C_{10}(\theta, \xi) &= C_{10} \left(1 - b_{10} \left(\theta - \theta_{ref} \right) / \theta_{ref} + d_{10} \left(\xi - \xi_{ref} \right) \right) \\
C_{01}(\theta, \xi) &= C_{01} \left(1 - b_{01} \left(\theta - \theta_{ref} \right) / \theta_{ref} + d_{01} \left(\xi - \xi_{ref} \right) \right) \\
C_{e10}(\theta, \xi) &= C_{e10} \left(1 - b_{e10} \left(\theta - \theta_{ref} \right) / \theta_{ref} + d_{e10} \left(\xi - \xi_{ref} \right) \right) \\
K_v(\theta, \xi) &= K_v \\
\eta(\theta, \xi) &= \eta_o \left(1 - bn \left(\theta - \theta_{ref} \right) / \theta_{ref} + dn \left(\xi - \xi_{ref} \right) \right) \\
\chi(\theta, \xi) &= \chi_o \left(1 - bc \left(\theta - \theta_{ref} \right) / \theta_{ref} + dc \left(\xi - \xi_{ref} \right) \right) \\
h(\theta, \xi) &= h \\
k(\theta, \xi) &= k
\end{aligned} \tag{57}$$

The constants used in this section are given in Table 1.

C_{10} (MPa)	b_{10}	d_{10}	C_{01} (MPa)	b_{01}	d_{01}	
0.268	0.1	10	0.237	0.1	10	
C_{e10} (MPa)	b_{e10}	d_{e10}	η_o (MPa.s)	bn	dn	
0.8256	0.1	10	0.129	0.1	10	
χ_o (MPa)	bc	dc	K_v (MPa)	α (K ⁻¹)	β	
0.0133	0.1	10	1000	10 ⁻⁴	10 ⁻³	
C_o (J.kg ⁻¹ K ⁻¹)	C_1 (J.kg ⁻¹)	ρ_o (kg/m ³)	k (W/m/K)	E_a (J/mol/K)	h	A_o
2000	10	1000	0.12	10 ⁵	10 ⁷	10 ¹⁶

Table 1: Material parameters of thermo-chemo-mechanical model

6.1 Adiabatic shear test

In this test, the shear specimen is assumed to be in plane strain (see Figure 5). The mechanical loading is sinusoidal with a constant amplitude (γ) and a frequency of 3Hz. The thermal load is applied in two steps: in a first step, a radiant heating of

5.10^5J is linearly applied, in a second step the radiant heating is set to zero. The initial temperature is 293°K and the initial degree of cure of this part is 0.6. The thermal flux is set to zero everywhere on the boundary of specimen (adiabatic condition).

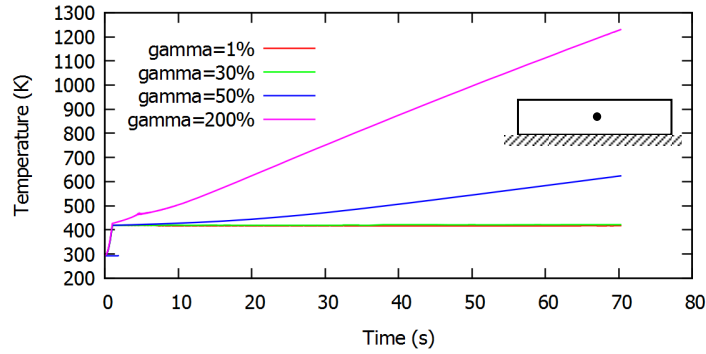


Figure 6: Temperature variation at the center of specimen upon time, for different mechanical amplitude of loading

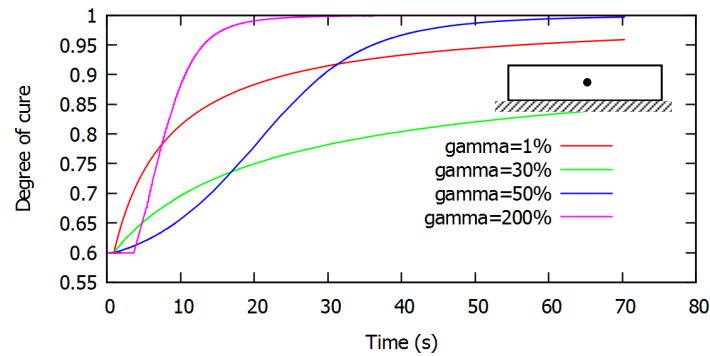


Figure 7: Degree of cure variation at the center of specimen upon time, for different mechanical amplitude of loading

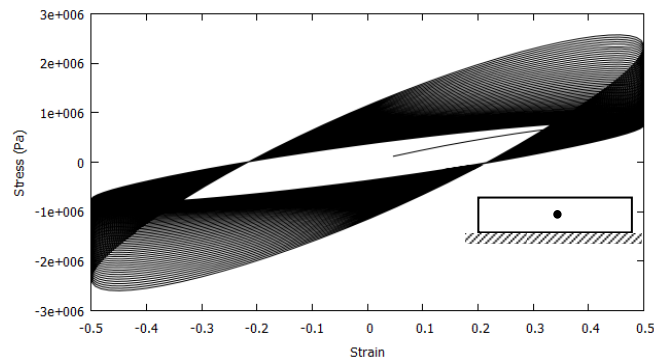


Figure 8: Evolution of hysteresis at the center of specimen upon time (for $\gamma = 50\%$)

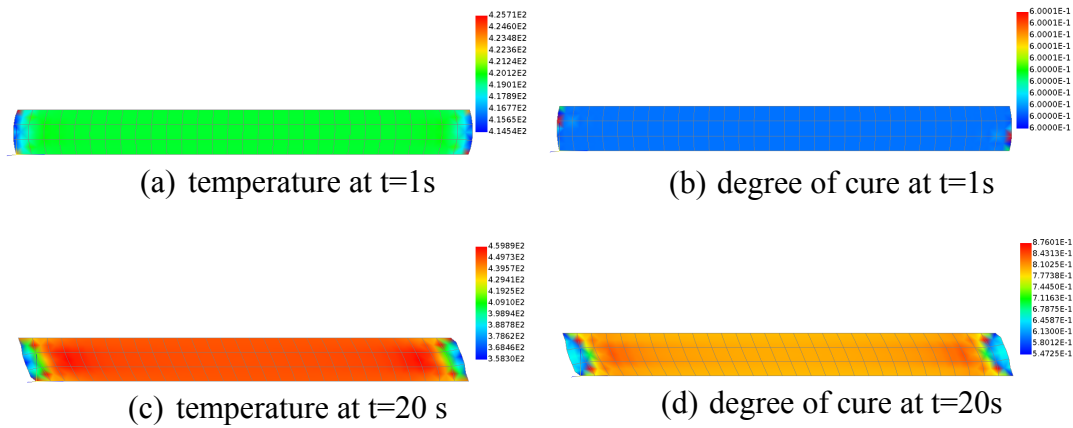


Figure 9: Evolution of the thermal and chemical fields.

Figures 6 and 7 show the evolution of the temperature and the degree of cure upon time for various mechanical amplitudes (from 1% to 200%) at the center of the specimen. It can be observed that the degree of cure, as expected, is strongly dependence on the mechanical loading. The mechanical amplitude affects both the induction time and the cure of time. On Figure 8, we show an example of mechanical response for 50% of simple shear amplitude. The mechanical behaviour shows a stiffness increase and more dissipation as the degree of cure increases (even if the temperature also increases). Figure 9 shows that the temperature field and the degree of cure field are nearly homogeneous excepted near the corners of specimen.

6.2 An isothermal example

In this test, the specimen is submitted to the shearing loading with isothermal condition in which we impose the constant temperature (293°K) on the boundary of specimen. The thermal load is also applied as the example above. The initial temperature is 293°K and the initial degree of cure of this part is 0.6.

Figures 10 and 11 show the evolution of the temperature and the degree of cure upon time for 50% of simple shear amplitude at the center of the specimen. We see after one second (when radiant heat term is set to zero) the increase of the temperature due to self-heating process. The induction time is longer than that of the adiabatic test and the cure time is shorter. Figure 12 shows mechanical response and we can see the same phenomenon as for the adiabatic test (stiffening and increase of dissipation). Figure 13 shows that the temperature field and the degree of cure field are heterogeneous. We also observe a smaller degree of cure and a smaller temperature near the corners than that of the center.

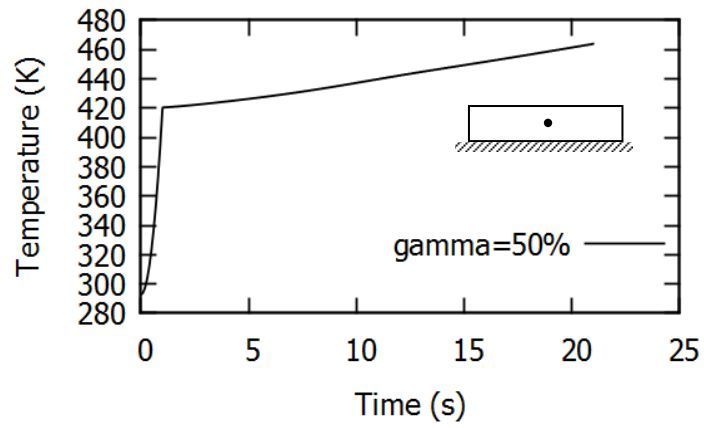


Figure 10: Temperature variation at the center of specimen upon time.

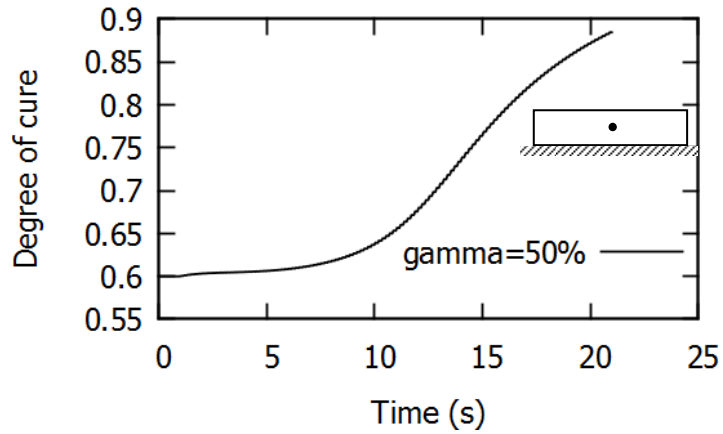


Figure 11: Degree of cure variation at the center of specimen upon time.

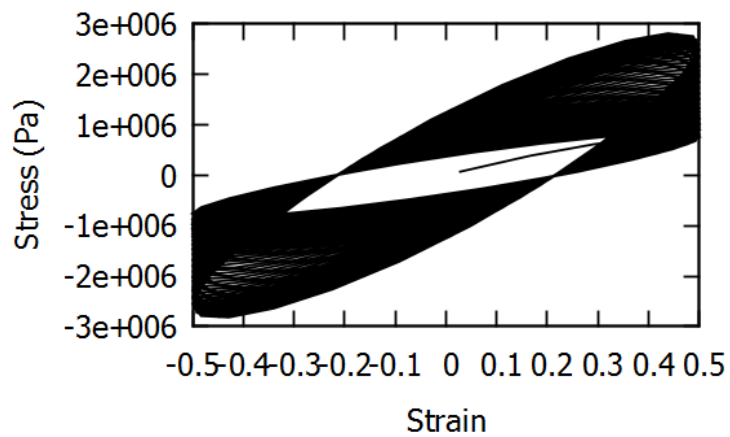


Figure 12: Evolution of hysteresis at the center of specimen upon time.

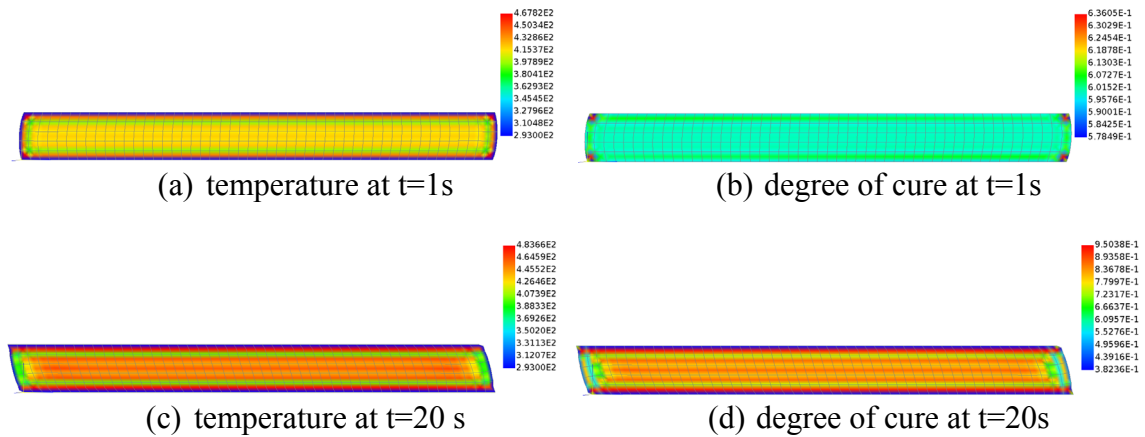


Figure 13: Evolution of thermal and chemical fields.

7 Conclusion

A new thermo-chemo-mechanical model has been proposed to simulate the evolution of the behaviour (thermal, chemical and mechanical) of filled rubber undergoing complex loadings. The proposed phenomenological approach is based on the decomposition of the volume variation in three parts and on the idea that some mechanical effects on the chemical evolution of the material exist. An original variational formulation and a finite element implementation have been developed. The main advantage of this framework is that it is general enough to be applied to a large class of materials and behaviour. We have shown that it is possible to build models that take into account complex thermo-chemo-mechanical coupling to explain experimental observations concerning post-curing. This approach could be naturally extended to many different domains of research: predicting aging or fatigue life, simulating rubber processing or accounting of non uniform rate of cure fields in rubber part. However, as there are only few experimental results available in the literature, in a short term, we will use this kind of model as a generic framework to define an original experimental campaign. Therefore, the influence of each coupling terms will be investigated from both the numerical and the experimental point of view.

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