DEVELOPMENT OF AN UEL SUBROUTINE IN ABAQUS FOR A FULLY COUPLED HEAT TRANSFER, MASS DIFFUSION AND STRESS ANALYSIS. IMPLEMENTATION TO ELASTIC POLYMERS.

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Abstract: In different industrial fields, polymer structures have to face high temperature and high gas pressure conditions, inducing gas adsorption and diffusion within them. A sudden drop in external pressure leads to an irreversible damaging of the material, due to the coupling of mechanical, thermal and gas diffusion effects. Even if this phenomenon was deeply investigated on an experimental point of view, the models that were carried out so far do not take all the different coupling possibilities into account. A thermo-diffuso-mechanical model was thus developed in the framework of the generalized standard media in order to build up more accurate prediction tools. It compares the system to an open homogeneous two-component continuous medium. This model was particularly applied to an elastic mechanical behavior of the material. Its numerical implementation in ABAQUS consisted in developing an UEL subroutine that takes the fully coupled thermo-diffuso-elastic behavior of the polymer into account. This should lead to a first qualitative estimation of the coupling effects.

1. Introduction

During the past twenty years, the use of polymers expanded widely in technical structures. In the petroleum industry for instance, numerous achievements were then made possible among which the one we particularly focus on: flexible pipes used for oil transportation. In operation, these structures have to face a wide range of stresses (100Mpa, 350-420°K) due to ambient environment and transported gas, which usually saturates the polymer sheath sealing of the conduit. When the pipe feeding stops, sudden drop of the inner pressure leads to damages in the sheath. This phenomenon is due to coupling between mechanical, thermal and gas diffusion effects. Such damage is of course unacceptable for sunk/buried pipes.

When one aims at foreseeing the in-service behavior of such sheaths, it becomes necessary to build predictive tools that enable global behavior to report. Thus, we developed a first simple and prospective model which gives back the behavior of a material subjected to mechanical loads, gas absorption and temperature gradient (either induced or due to the outer medium). The implementation of such a model in

ABAQUS was restricted to elastic material. A first qualitative estimation of the thermo-diffuso-mechanical coupling is thus possible.

This paper presents the basics of the thermo-diffuso-elastic model as well as the main features of its development in ABAQUS. Numerical results will be presented during the conference.

2. Presentation of the problem

Generally speaking, a high-pressure gaseous environment leads to gas adsorption then diffusion within the material it is contacted with. Polymers are subjected to such a phenomenon, which induces the material dilatation and alteration of its mechanical properties. When the outer pressure is suddenly released, namely an explosive decompression, gas which is trapped within the material tends to expand and diffuses toward the outer medium correspondingly (at least often) inducing a local decrease in temperature. Irreversible mechanical damage generally appears as consequence of coupling between mechanical, thermal and diffusion effects. Based on the nature of gas-polymer system, decompression rate, thermal conditions, such damage appear either locally as cracks or in a diffuse way as foam.

On an experimental point of view, this phenomenon was subjected to numerous studies. Two examples are given hereafter for information. A study carried out by Lorge (1999) reports the behavior of polyvinylidenefluoride subjected to explosive decompression in a carbon dioxide environment. For several types of polymer, Dewimille's work (1993) highlights the nature of damage caused by decompression as well as the modification of global mechanical behavior, which is associated to this phenomenon.

On a theoretical point of view, the three aspects were generally discussed separately: mechanical problem, thermal problem or diffusion problem. The literature shows a certain amount of mathematical models for diffusion, based on statistical thermodynamic, and which differ from one another in the choice of internal variables (Doghieri, 1996). It is important to note that these models do not make it possible to translate the thermo-diffuso-mechanical coupling.

On a numerical point of view, a first modeling of such a phenomenon was proposed. For instance, Jarrin's and Gaillard-Devaux's works (respectively 1994 and 1995) define a first damage criterion based on simplifying hypotheses. Nevertheless, the alterations of mechanical properties due to impregnation as well as temperature variation that occur during decompression are not taken into account. Coupling is moreover only partially discussed. Actually, ABAQUS provides the *COUPLED TEMPERATURE-DISPLACEMENT option for analyzing thermo-mechanical or diffuso-mechanical problems with the possibility of considering respectively the diffusion or temperature effects on the mechanical and thermal or diffusion properties. But, the fully coupled, simultaneous heat transfer, mass diffusion and stress analysis is not possible.

As a first step, we found important to build a global model that takes into account the whole coupling panel (mechanical, thermal and diffusive couplings). Therefore, the generalized standard media were considered. As a second step, the development of an UEL subroutine was necessary. In order to simplify this model implementation in ABAQUS, a purely elastic problem was considered. Such a simplification will obviously not make it possible to bring face to face the computation and experimental results on a quantitative point of view, but will enable qualitative comparison of the coupling effects.

3. System representation: gas and polymer mixture

3.1 Thermodynamic framework

The model set-up is carried out in the framework of generalized standard media and therefore follows a classical approach. A field of state variables represents the material behavior. Introduction of a first potential (specific free energy) makes it possible to set laws linking thermodynamic forces (stress, entropy, chemical potential) to dual variables (strain, temperature, normalized concentration). The dissipations that are only associated to thermal and diffusion phenomena in an elastic behavior case are discussed using a second potential (dissipation potential). This potential expression depends on the envisaged coupling (fully or not). Once defined, the potential expression leads to complementary evolution laws (Fourier's, Fick's). These different steps are presented in the following paragraphs.

In this thermodynamic framework, every elementary representative volume (ERV) is considered at the macroscopic scale to be a bi-component continuous, homogenous medium: polymer and gas. Therefore, the volume characterization can be carried out using average physical value based on each specie's value. One focuses on the average behavior of the medium.

Moreover, this ERV is open and thus trades heat power with the surrounding medium as well as matter. The two-species' diffusion is a molecular diffusion, which obeys a Fick's type law and then is driven by concentration gradients. The sorption mode that is associated to each specie obeys a Henry's law at the domain boundary.

Besides, the material is assumed to be isotropic and is only studied in the framework of small perturbations. Finally, a strong development assumption leads to associate each ERV characterization magnitude to a constant value in time and space. This latter approximation is by no means verified but makes it possible to strongly simplify the equations.

3.2 Local equations

The behavior of polymer subjected to pressure, gas concentration as well as temperature variation is driven by diffusion, dynamic and thermal equations. The two first equation families can be classically set up but the third thermal one is not so easy since it must embed couplings corresponding to dissipative phenomena.

3.2.1 Mass balance

In a bi-component system where no chemical reaction occurs within it, each specie's mass remains separately the same, which leads to two mass balance equations.

The species put together are described by the following variables:

- ρ average mixture mass density (kg/m^3).

- C_i normalized concentration of the ith constituent (N/m²) and defined as the rate between concentration (ppm, i.e. mg/kg) and solubility coefficient S_i (ppm.m^2/N).

- $\vec{J}_{mi}$ relative mass flux of the i diffusing phase (kg/m².s).

Mass balance for i^{th} component leads to the following diffusion equation:

$$\rho \; 10^6 \; S_i \; \frac{dC_i}{dt} \; = \; - \; \mathrm{div} \; \vec{J}_{mi} \; .$$

This classical balance equation is applied to polymer and gas. Nevertheless, for flux and normalized concentrations, the following equations come true by definition:

$$\vec{J}_{mg} \; = \; - \; \vec{J}_{mp} \quad \text{and} \quad S_g \; \frac{dC_g}{dt} \; = \; - \; S_p \; \frac{dC_p}{dt} \; .$$

Both the diffusion equations are linked and thus only the gas one will be used further in this document:

$$\rho \; 10^6 \; S_g \; \frac{dC_g}{dt} \; = \; - \; \mathrm{div} \; \vec{J}_{mg} \; . \tag{1}$$

3.2.2 Mechanical balance

The balance equations are derived from fundamental principle of dynamics. When one neglects the inertia effects ($\rho \vec{\gamma} \approx \vec{0}$), mechanical balance leads to the following motion equation:

$$\vec{\mathrm{div}} \; \underline{\underline{\sigma}} \; + \; \rho \vec{f} \; = \; \vec{0} \; , \tag{2}$$

where $\underline{\underline{\sigma}}$ is the total Cauchy stress tensor (N/m^2), $\vec{f}$ is the body force at any point within the ERV per unit of mass (N/kg) and $\vec{\gamma}$ the considered particle acceleration (m/s²).

3.2.3 Thermodynamic balance – First and Second laws

   a.   Thermodynamic potential, equations of state

It is classically seen in continuous media thermodynamic to introduce the specific free energy ψ of the mixture (J/kg). For an elastic behavior this potential depends on three state variables: the temperature T (°K), the infinitesimal strain tensor $\underline{\underline{\varepsilon}}^e$ and the gas and polymer normalized concentrations C_g and C_p, respectively.

$$\psi \; = \; \psi(\underline{\underline{\varepsilon}}^e, T, C_g, C_p) \; .$$

When a normal configuration is assumed and when one considers the first two thermodynamics laws, system behavior laws also known as equations of state can be derived from ψ. When specific entropy is denominated s (J/kg.°K), mass chemical potential for i specie (dual variable of the mass fraction) is denominated μ_i (J/kg), one can write down these laws as follows:

$$\underline{\underline{\sigma}} = \rho \left(\frac{\partial \psi}{\partial \underline{\underline{\varepsilon}}^e} \right)_{T, C_g, C_p} \quad , \quad s = - \left(\frac{\partial \psi}{\partial T} \right)_{\underline{\underline{\varepsilon}}^e, C_g, C_p} \quad \text{and} \quad \mu i = \frac{10^{-6}}{S_i} \left(\frac{\partial \psi}{\partial C_i} \right)_{T, \underline{\underline{\varepsilon}}^e, C_{k \neq i}} \quad .$$

Remark: $\left(\frac{\partial \cdot}{\partial \cdot} \right)_*$ means partial derivation with * as constant value.

When one considers the small perturbations, that is to say infinitely small strains and small differences of temperature and normalized concentration, the development of potential ψ to the second order make it possible to build the following linear behavior laws:

$$\underline{\underline{\sigma}} = \underline{\underline{\sigma}}_o + \lambda \, (\, \text{tr} \, \underline{\underline{\varepsilon}}^e \,) \underline{\underline{I}} + 2 \mu \, \underline{\underline{\varepsilon}}^e - (3 \lambda + 2 \mu) [\, \alpha_T \, (T - T_o) + (\alpha_g - \alpha_p) 10^6 \, S_g \, (C_g - C_g^o)] \underline{\underline{I}} \quad (3)$$

$$s = s_o + \frac{1}{T_o} \, C_{\underline{\underline{\varepsilon}}^e, C_i} \, (T - T_o) + \frac{1}{\rho} \, (3 \lambda + 2 \mu) \alpha_T \, (\, \text{tr} \, \underline{\underline{\varepsilon}}^e) + D_1 \, 10^6 \, S_g \, (C_g - C_g^o) \quad (4)$$

$$\mu_g - \mu_p = (\mu_g^o - \mu_p^o) + D_2 \, 10^6 \, S_g \, (C_g - C_g^o) - \frac{1}{\rho} \, (3 \lambda + 2 \mu) (\alpha_g - \alpha_p) \, \text{tr} \, \underline{\underline{\varepsilon}}^e - D_1 \, (T - T_o) \quad (5)$$

where:

- T_o , c_i^o , $\underline{\underline{\sigma}}_o$, s_o and μ_i^o respectively represent initial temperature, normalized concentration of the ith constituent, stress, specific entropy and chemical potential at zero strain, thermal and mass differences.

- $C_{\underline{\underline{\varepsilon}}^e, C_i} = T \left(\frac{\partial s}{\partial T} \right)_{\underline{\underline{\varepsilon}}^e, C_g, C_p}$ is the specific heat at constant strain and normalized concentration (J/kg.°K).

- λ and μ are the Lamé elastic coefficients (N/m²).

- α_T (°K), α_g and α_p are the isotropic expansion coefficients linked to respectively heat, gas and polymer transfer.

- The effect of temperature variation (concentration variation) on the chemical potential (entropy) is linked to D_1 coefficient (J/kg.°K).

- D_2 is defined as function of coefficients $\lambda, \mu, \alpha_g, \alpha_p, \rho, A_D$ and B_{DM} , the two latter ones being defined further in the document (m²/s²).

- $\underline{\underline{I}}$ is identity matrix.

b. Heat transfer equation

Let $\vec{J}_q$ (J/m².s) be the heat flux per unit area, following into the ERV, and r (J/m³.s) the volume density of heat generated externally for instance by an radiating source into, the heat balance equation taking into account the different couplings has the following shape:

$$\rho \; C_{\underline{\underline{\varepsilon}}^e, C_i} \frac{dT}{dt} = -\operatorname{div} \vec{J}_q + r - (3\lambda + 2\mu)\,\alpha_T\,T\;\operatorname{tr}(\frac{d\,\underline{\underline{\varepsilon}}^e}{dt}) - \rho\left[T\,D_1 + (\mu_g - \mu_p)\right] 10^6 \; S_g \frac{dC_g}{dt} \qquad (6)$$

The last part of it corresponds to temperature variation linked to gas diffusion within the polymer material.

Remark: tr represents the trace operator.

c. Dissipations

Thermodynamics Second law makes it possible to define the volume dissipation φ (positive or nil) linked to entropy generation. An elastic behavior is characterized by the fact that it has no internal variables, which leads to a nil intrinsic dissipation. φ is split into two contributors, φ_1 and φ_2 (J/m³.s), which are linked to respectively the temperature and chemical potential gradients, so that:

$$\varphi = \varphi_1 + \varphi_2 \geq 0 \;\;, \;\; \varphi_1 = -\vec{J}_s \;.\; \overrightarrow{\operatorname{grad}}\,T \;\; \text{and} \;\; \varphi_2 = -\vec{J}_{m_g} \;.\; \overrightarrow{\operatorname{grad}}\,(\mu_p - \mu_g) \,,$$

where:

$$\vec{J}_s = \frac{1}{T}\,(\vec{J}_q - \sum_{i=1}^{2} \mu_i\,\vec{J}_{m_i})$$

is the entropy flux (J/s.°K.m^2).

Compliance with Second laws leads to the definition of a dissipation potential d and its dual d* (through Legendre-Fenchel transformation) (J/m³.s). Depending on the considered coupling assumptions, these scalar value, continuous, convex and positives functions have a different expression. Evolution equations are given depending on how d* is considered in the following paragraph.

d. Coupling processing

In case of a total coupling between dissipative phenomena, the dual potential turns to be a unique function, which is given by equation 7. When the normal dissipativité assumption is done, one sets the evolution complementary equations corresponding to equation 8.

$$d^* = d^*(-\overrightarrow{\operatorname{grad}}T, -\overrightarrow{\operatorname{grad}}[\mu_g - \mu_p]) \qquad (7)$$

$$\vec{J}_s = \left(\frac{\partial\, d^*}{\partial\,(-\overrightarrow{\operatorname{grad}}T)}\right)_{-\overrightarrow{\operatorname{grad}}(\mu_g - \mu_p)} \;\;,\;\; \vec{J}_{m_g} = \left(\frac{\partial\, d^*}{\partial\,(-\overrightarrow{\operatorname{grad}}[\mu_g - \mu_p])}\right)_{-\overrightarrow{\operatorname{grad}}T} \qquad (8)$$

Moreover, when the dissipation phenomena are assumed to be driven by linear and fully coupled laws, the potential d* has a quadratic form and lead to the following law let us assume the isotropic hypothesis and the formerly stated expression of the chemical potential (equation 5):

$$\vec{J}_{mg} = -A_D \, 10^6 \, S_g \, \vec{grad} \, c + B_{DM} \, \vec{grad} \, [tr \, \underline{\underline{\varepsilon}}^e \,] + A_{TD} \, \vec{grad} \, T$$

$$\vec{J}_q = -[\,B_{TD}\,T - A_{TD}(\,\mu_g - \mu_p)]\,\vec{grad}T - [\,D_2 \, C_{T\mu}T + A_D(\,\mu_g - \mu_p)]\,10^6 \, S_g \, \vec{grad}c + [\,A_{DM} \, C_{T\mu}T + B_{DM}(\,\mu_g - \mu_p)]\,\vec{grad}[tr \, \underline{\underline{\varepsilon}}^e\,]$$

where:

- A_D is defined to be the product between the diffusion coefficient and the average mixture mass density (kg/m.s)

- B_{DM} corresponds to the volume deformation gradient effect on mass flux (kg/m.s)

- A_{DM} is based on $\lambda, \mu, \alpha_g, \alpha_p$ and ρ coefficients (m^2/s^2)

- D_2 which was formerly introduced is expressed as a function of the following coefficients: $\lambda, \mu, \alpha_g, \alpha_p, \rho, A_D$ and B_{DM} (m^2/s^2).

- A_{TD} corresponds to the temperature gradient effect on the mass flux (kg/m.s.°K)

- B_{TD} is a coefficient defined out of the former coefficients (W/m.°K²)

When the total dissipative processes decoupling is assumed, two dual potentials d_1^*, d_2^* compliant with the normality assumption are used:

$$d^* = d_1^*(-\vec{grad}\,T) + d_2^*(-\vec{grad}\,[\,\mu_g - \mu_p]) \, .$$

As formerly stated, an important simplification of these equations consists in considering a quadratic form, defined as positive, as the dual dissipation potential. One can then recognize well-known evolution equations, namely Fourier's and Fick's when a simple conduction case is considered for the first one and a diffusion case is considered for the second one:

$$\vec{J}_s = -k_T \, \vec{grad} \, T \quad \text{and} \quad \vec{J}_{mg} = -k_\mu \, \vec{grad} \, (\mu_g - \mu_g)$$

where k_T is defined as the rate between thermal conductivity and temperature (J/m.s. °K²) and k_μ is easily expressed as a function of B_{DM} and A_{DM} (kg.s/m³).

    e.   Summary: assessment of the problem unknown values

The variables defining the thermo-diffuso-mechanical state or more precisely the thermo-chemico-mechanical state of the material (gas-polymer mixture) are the components of strain vector (u, v, w for a 3D model and u, v for a 2D model), the temperature T and normalized gas concentration C_g . Among all

the different coefficients that were introduced, B_{DM} and A_{DM} are the only ones still to be determined through a parametric study.

4. Development of an UEL subroutine

4.1 General processing

The model implementation in ABAQUS led to program an UEL subroutine, in which element's contributions to the residual in one hand and to the Jacobian in the other hand were defined respectively by:

$$\{F\} \quad \text{and} \quad [K] = -\left(\frac{\partial\{F\}}{\partial\{q_n\}}\right) - \frac{1}{\Delta t}\left(\frac{\partial\{F\}}{\partial\{\dot{q}_n\}}\right),$$

where $\{q_n\}$ represents the vector of nodal unknown variables associated to the n-node element of the following dimension:

- $5n \times 1$ when three dimensions are considered

$$^T\{q_n\} = \{u_1, v_1, w_1, u_2, v_2, w_2 \dots u_n, v_n, w_n, T_1, T_2 \dots T_n, C_1, C_2 \dots C_n\}.$$

- $4n \times 1$ when two dimensions are considered

$$^T\{q_n\} = \{u_1, v_1, u_2, v_2 \dots u_n, v_n, T_1, T_2 \dots T_n, C_1, C_2 \dots C_n\}.$$

A weak formulation based on the former equations was thus proposed for each problem (mechanical, thermal and diffusive) considered separately. The spatial and temporal discretization of these three formulations led to the three following contributions to the residual:

$$\{F^m\} = \{F^m\}(\{q_n\}) \quad, \quad \{F^T\} = \{F^T\}(\{q_n\}, \{\dot{q}_n\}) \quad \text{and} \quad \{F^g\} = \{F^g\}(\{q_n\}, \{\dot{q}_n\}).$$

The global contribution is thus gotten through composition of the former vectors:

$$\{F\} = \{F\}(\{q_n\}, \{\dot{q}_n\}) = \begin{Bmatrix} \{F^m\} \\ \{F^T\} \\ \{F^g\} \end{Bmatrix}$$

and its derivation led to build the element's contribution to the Jacbian:

$$[K] = -\left(\frac{\partial\{F\}}{\partial\{q_n\}}\right) - \frac{1}{\Delta t}\left(\frac{\partial\{F\}}{\partial\{\dot{q}_n\}}\right) = \begin{bmatrix} [K^{mm}] & [K^{mT}] & [K^{mg}] \\ [K^{Tm}] & [K^{TT}] & [K^{Tg}] \\ [K^{gm}] & [K^{gT}] & [K^{gg}] \end{bmatrix}.$$

In this matrix, the non-diagonal terms correspond to the different couplings. The subscripts 'm', 'T' and 'g' indicate the mechanical, thermal and diffusion processes, respectively. Note that this array is not symmetric and thus requires the introduction of UNSYMM parameter.

4.2   Remarks about spatial discretization

An iso-parametric interpolation was chosen, in other words the same interpolation for geometry and unknown fields (displacements, temperatures and normalized concentrations). The proposed elements are of three kinds:

- 6-node triangle

- 4- and 8-node tetrahedron

- 8- and 20-hexahedron

with for two-dimensional elements a specific process for plane stress, plane strain and axisymmetric problems.

4.3   Remarks concerning external loading

Mechanical loads as volume, surface or pinpoint force and imposed displacement may act on the ERV all along the step.

On a thermal point of view, the ERV may be subjected to an outer radiating source. Thermal flux as well as temperature may be set at one given point or at part of the boundary. Finally it may be subjected to surface flux (thermal convection, conduction or radiation) defined by the following relations:

$$\vec{J}_q \cdot \vec{n} = -h_c\ (\,T_a - T\,) \quad \text{and} \quad \vec{J}_q \cdot \vec{n} = -h_r\ (\,T_a^4 - T^4\,)\,,$$

where $\vec{n}$ is the unit outward normal to the surface, T_a being the ambient temperature, h_c and h_r being the thermal conduction/convection and radiation coefficients.

In the same way, normalized concentration or matter flux may be applied to the whole REV boundary or punctually applied. Particularly, diffusion surface flux being compliant with:

$$\vec{J}_{mg} \cdot \vec{n} = -h_{dif}\ (\,C_a - C\,)$$

was also taken into account, C_a being the normalized concentration in the ambient medium and h_{dif} the associated coefficient.

5. Prospects

The first numerical modeling we intend to carry out aims at getting a qualitative definition of the thermo-diffuso-mechanical coupling effects and at evaluating the magnitude of both the unknown coefficients through parametric study. The structures we intend to test will be subjected to pressure (thus concentration) and/or temperature variations. One will estimate how the coupling parameters have influence on the structure's response by letting them vary. These results will be presented during ABAQUS User's conference.

A thermo-diffuso-visco-elastic model based on Zener's rheology is currently being developed. We expect it to bring out a good representation of mechanical behavior of polymer subjected to small strain. Then this model will also be translated in an UEL subroutine. Comparison between numerical and experimental results will make it possible to get a quantitative estimation of the coupling.

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