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A two-phase model for the diffuso-mechanical behaviour of semicrystalline polymers in gaseous environment

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ABSTRACT

The increasing use of semicrystalline polymers (SCPs) in complex petroleum structures which are subjected to high variations of temperature and gas pressure requires the development of reliable and predictive constitutive models. For that purpose a diffuso-elastoviscoplastic model is presented here by considering a two-phase representation, classically used in porous media, for the representative volume element (RVE) of SCP in gaseous environment. One phase is crystalline (skeleton), and the other corresponds to the mixture (fluid) of gas and free amorphous (the latter is considered penetrable by gas). The modelling is described within the framework of the thermodynamics of irreversible processes with internal variables. General balance equations are established by considering the above RVE. The general diffuso-mechanical macroscopic continuum formulation obtained is applied to elastoviscoplastic behaviour. The implementation of this two-phase diffuso-elastoviscoplastic model in Abaqus™ software via a user subroutine allows to study the interactions between crystal, free amorphous and gas during a rapid decompression test. More precisely, the evolution of pressure in the two-phase polyvinylidene fluoride SCP is given during a decompression test with carbon dioxide. Some results are discussed. The presented model is supposed to facilitate the introduction of damage criterion in order to describe the blistering occurring during a decompression.

1. Introduction

In petroleum transportation polymers are used as seal barriers in flexible pipes. In this context, they are supposed to resist to high pressure (until 100 MPa) of aggressive chemical fluids like hydrogen sulphide or carbon dioxide (CO_2), at service temperature ranging from 70 to 130 °C. Semicrystalline polymers (SCPs) such as polyethylene or polyvinylidene fluoride (PVF_2) are selected in this context due to their chemical inactivity and their mechanical proper ties in a broad range of temperature and pressure (Dewimille et al., 1993). They are subjected to phenomenon of blistering which is a damage mode due to high decompression rate in the flexible pipe. Indeed, under the pipe service pressure, gas saturates the polymer sheath of the flexible. This sheath is liable to sudden operating interruptions, resulting in a high drop of pressure in the pipe. So, gas present in the polymer sheath tends to diffuse outside the material and leads to the damage of the SCP (Meimon, 2000). Mechanisms inducing various forms of damage, cracks or blisters, e.g., are complex and depend on the gas-polymer system. For the same system, the damage mode can vary with the decompression rate. Damage is generally a consequence of high interactions between thermal, diffusion and mechanical phenomena (Gaillard-Devaux, 1995;Boyer, 2003). It is thus necessary to predict the risks of initiation of damage in order to design structures including SCPs in gaseous environment and to reasonably predict their life time. Currently there is no model able to deal with this damage problem.

In literature, some authors have recently developed thermo-diffuso-mechanical models in order to describe the behaviour of polymers in gaseous environment. For instance, Rambert and Grandidier (2005) have proposed a thermo-diffuso-viscoelastic model which was supposed to be extended further to treat damage, as discussed above. The abilities of the elastic model have been evaluated in a previous article (Rambert and Grandidier, 2005). However, the extension of the mixture theory based Rambert's model cannot be reasonably considered to incorporate blistering because in this approach the microstructure description is too poor. To sum up, this fully coupled elastic approach does not explain the damage initiation because the polymer and the gas are modelled thanks to a perfect mixture. Consequently, the microstructure effect on damage initiation is not taken into account. Indeed, it is essential to deal with the SCP microstructure for two fundamental reasons. First, most of the study about gas diffusion in SCP concluded that gas diffusion takes place only in the amorphous phase (Michaels and Bixler,

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1961a and Michaels and Bixler, 1961b;Michaels and Parker, 1959), which is not accounted for in Rambert's model.

Moreover, independently of their behaviour in gaseous environment, SCPs have a complex mechanical behaviour which depends on their microstructure (Cangémi and Meimon, 2001). Various approaches of scale transition (Nikolov and Doghri, 2000;Nikolov et al., 2002; Van Dommelen et al., 2003a; Van Dommelen et al., 2003b) have been developed in order to deduce mechanical behaviour of SCPs using a cell composed of several crystalline lamellae stacked. Scale transition approaches are very interesting but come up against theoretical and numerical difficulties for viscoelastic and/or elastoviscoplastic polymers. In order to get around these difficulties the elastoviscoplastic (VISCOPOL) model has been developed at the French Institute of Petroleum (IFP) (Cangémi and Meimon, 2001) at a mesoscopic scale; it represents a sort of compromise between theoretical difficulties and modelling scope. The VISCOPOL model distinguishes in a simple way the two phases of a SCP, the 'solid' (crystal, confined amorphous) and the 'fluid' (free amorphous) phases. This model has been developed in order to describe the SCP mechanical behaviour. Comparisons with experimental data have been realized in Cangémi and Meimon, 2001 and the VISCOPOL model exhibits good abilities to predict SCP triaxial behaviour under several history loads and more particularly with PVF_2. Its advantage is to provide an estimation of mean stress applied to crystal and to amorphous phase.

The objective of the present contribution is thus to *reconsider* the VISCOPOL model by taking into account the presence of gas in the free amorphous phase. The interaction between amorphous and gas should be described in order to estimate the stress in amorphous phase and to quantify the risk of damage initiation during blistering test. It is clear that we do not have any experimental information on SCP behaviour under high pressure of CO_2. The model is built with the aim of reducing the number of adjustable or identifiable parameters. To achieve it, one specific physical description is proposed. Previously, diffusion phenomena are modelled at the scale of a spherolyte and mechanical behaviour is established in a rigorous thermodynamic framework.

In this paper, assuming that gas diffusion takes place only in the free amorphous, the representative volume element (RVE) of SCPs in gaseous environment corresponds to that of the VISCOPOL model in which gas is introduced in the fluid phase. The latter is represented by a homogeneous non-reacting gas-free amorphous mixture. We opt for the classical framework of the thermodynamics of irreversible processes with internal variables. The assumptions of small deformation and isotropy are put forward. Moreover, thermodynamic potentials are chosen quadratic so that constitutive (state) laws are linear. In this framework, we obtain coupling between diffusion and mechanical phenomena which gives the interactions between gas, free amorphous and crystal. The interest of this present approach is to develop a model for SCPs in a gaseous environment which can be extended later to take into account the damage of SCPs in a gaseous environment.

The paper is organized as follows: in Section 2, the model RVE is presented. The general two-phase diffuso-mechanical model based on the classical internal variable framework is described. The specific internal variables are not yet detailed in order to conserve the general nature of the modelling. In Section 3, the specific diffuso-elastoviscoplastic behaviour involving coupling between solid and gas-free amorphous phases is detailed. The implementation of this two-phase model is made in the engineering finite element Abaqus™ software via a user subroutine UEL (User Element). In Section 4, some selected numerical simulations are presented. They concern in particular pressure levels in both phases of a PVF_2 specimen subjected to rapid CO_2 decompression.

2. General formulation of the model

The modelling proposed in this paper is based on the mechanics of porous continua (Coussy, 1995). Indeed, the RVE chosen for SCP in gaseous environment is based on a two-phase representation classically used in the context of porous media: one phase is crystalline (skeleton), and the other corresponds to the mixture (fluid) of gas and free amorphous. Considering this RVE, general balance equations are established within the formal framework of the thermodynamics of irreversible processes with internal variables.

2.1. Definition of the representative volume element

Within the VISCOPOL model framework, only two phases are considered in a SCP. According to their mechanical characteristics, the first one consists of crystalline lamellae surrounded with amorphous phase in a confined (or 'glassy') state. The stiffness of crystalline lamellae and their surroundings is high, the behaviour of this phase is thus considered as that of a 'solid'. The second phase consists of free amorphous, its behaviour is supposed to be that of a 'fluid' (Fig. 1). Indeed, the free amorphous phase has a relatively weak stiffness with regard to the precedent one. This 'fluid' phase is characterized by a high intrinsic mobility. Thanks to these considerations the SCP microstructure can be correctly represented, at a macroscopic scale, by the superposition of two continuous media: the 'solid' and the 'fluid' (Fig. 1).

In this paper, assuming that gas diffusion takes place only in the free amorphous, the RVE of SCP in gaseous environment corresponds to that of the VISCOPOL model in which the gas is introduced in the fluid phase (Fig. 2). The latter is now represented by a homogeneous non-reacting gas-free amorphous mixture (Fig. 2).

Note that if it is not clearly specified, the developments below refer to this RVE, which is considered here in its reference configuration. In the continuation of this document, the fluid phase is also named mixture, the free amorphous is simply called amorphous and the solid phase is also named skeleton.

2.2. Definition of the mass fractions

The mixture is defined by relations (1) and (2) below which are satisfied at any time. Y^i $(i = \mathrm{fl}, \mathrm{g}, \mathrm{a})$ denotes the mass fractions of fluid (fl), gas (g) and amorphous (a) relatively to the whole of the system. $Y^{\mathrm{g/fl}}$, $Y^{\mathrm{a/fl}}$ define the mass fractions of gas and amorphous relatively to the fluid phase which are noted $\mathbf{Y}^{\mathrm{g/fl}}$ and $\mathbf{Y}^{\mathrm{a/fl}}$ in the actual configuration. The latter are linked by relation (3).

Parameter ϕ_o (2) is the initial connected porous fraction, ρ_o (kg/m^3) is the average density of the gas–SCP system and $\rho_\mathrm{o}^{\mathrm{fl}}$ (kg/m^3) is the initial density of the mixture. Note that the mass fraction of the skeleton is defined by Y^{sq} and that all the mass fractions defined here do not have unit.

$$Y^{\mathrm{fl}} = Y^{\mathrm{g}} + Y^{\mathrm{a}}, \tag{1}$$

$$\phi_\mathrm{o}\rho_\mathrm{o}^{\mathrm{fl}}Y^{\mathrm{g/fl}} = \rho_\mathrm{o}Y^{\mathrm{g}}, \tag{2a}$$

$$\phi_\mathrm{o}\rho_\mathrm{o}^{\mathrm{fl}}Y^{\mathrm{a/fl}} = \rho_\mathrm{o}Y^{\mathrm{a}}, \tag{2b}$$

$$\mathbf{Y}^{\mathrm{g/fl}} + \mathbf{Y}^{\mathrm{a/fl}} = 1. \tag{3}$$

2.3. Balance of mass

The statement of balance of mass contains three parts: first the gas–SCP system is considered as a whole, then each phase is treated separately and finally, each constituent (free amorphous, gas) of the fluid phase is studied. The balance for each phase (Eqs. (4) and (5)) and each constituent (Eqs. (6) and (7)) is given below. In