BEHAVIOUR AND FRACTURE OF POLYETHYLENE AT HIGH TEMPERATURE UNDER HIGH PRESSURE OF METHANE.

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To study the damage mechanisms and the fracture in a low density polyethylene used for the sheathing of flexible pipelines, several specimen geometries were tested. The experiments consist of a saturation with methane up to a pressure of 10MPa at high temperature (e.g.70 and 100°C) followed by a rapid decompression of samples. The experimental damage was located and quantified from both optical and scanning electronic microscopy (SEM) observations using image analysis possibilities. An attempt is proposed to modelling the different phases of the rapid decompression. The crack initiation criterion is based on the local maximum shear stress. The numerical calculations are in good agreement with the experimental results.

INTRODUCTION

Polymeric materials used in the petroleum industry are often placed in contact with gases at temperature up to 100°C and pressure up to 100 MPa. This is the case for elastomeric seals as well as for the thermoplastic materials used for the sheathing of flexible pipelines (polyethylene, polyamide or fluorinated polymers). Then, these polymers can absorb methane at high temperature under high pressure. If a rapid decompression occurs, the gas can either diffuse out of the material or expand and thus damage the polymer forming cracks and cavities.

To study the damage mechanisms and the fracture in a low density polyethylene used for the sheathing of flexible pipelines, several specimen geometries were tested. The experiments consist of a saturation with methane up to a pressure of 10MPa followed by a rapid decompression of samples with rates from ten seconds to several minutes. The thickness and the temperature of the specimens were measured with sensors. The damage was located and quantified from both optical and electronic microscopy observations using image analysis possibilities. These experimental data are used to model both damage and crack initiation of this polyethylene.

To simulate the different phases of the tests (damage and crack initiation), an analogy is made on the one hand between the expansion of the material with gas sorption and a thermal dilatation, and on the other hand, between the explosive

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decompresion of the samples and a thermal shock. Using the Abaqus code for the simulation, we have taken into account the effect of the gas sorption on the mechanical properties of the material.

The crack initiation criterion is based on the local maximum shear stress. This criterion is applied to predict the explosive decompression conditions of different specimen geometries. The numerical calculations are in good agreement with the experimental results.

EXPERIMENTAL PROCEDURES

Explosive decompression tests. High-pressure cell equipped with temperature, pressure and displacement sensors have been used to evaluate the behavior of the compression-molded low density polyethylene considered in this paper. After introduction of samples inside the cell, the temperature and pressure are regulated to setpoint values during enough time to allow a complete diffusion of the methane in the samples thickness. This time of saturation can vary from a few hours to a few days depending on the temperature of the tests. This time is estimated on the basis of the permeability measurements. After complete saturation of the samples, the pressure is released throught a valve. The temperature and pressure variations of the gas are recorded during the decompression phase. The LVDT sensor measure the thickness variation of the samples during both diffusion of methane up to the setpoint values and explosive decompression. About 30 minutes after decompression is finished, the cell was opened and the samples were controled. The first control was visual or by optical microscopy. The density of the samples was measured by a balance. In some cases, the density change, due to the cracks (blisters) or bubbles inside the samples. Then image analysis was used to locate the blisters in the thickness of the cutted samples and quantify the blisters shape, their orientation and their number in each cut samples. A more local examination was then performed by SEM to determine the state of the material in the blisters. The details of the experimental procedures are given elsewhere (E. Devaux (1)).

Permeability, diffusivity and solubility of methane and mechanical properties of low density polyethylene under both pressure and temperature. The coefficients of solubility, diffusivity and permeability throught the materials are obtained using the weight loss method. We consider that, for the pressures lower than 10 MPa, there is no dependance of the gas concentration on the coefficient of diffusion.

The bulk modulus K of the material under pressure have been measured by a Pressure-Volume-Temperature PVT apparatus working as a dilatometer. Futhermore, the tensile properties come from a standard Instron machine equipped with a temperature control chamber. The Young's modulus E is given by the relationship :$K=E/3(1-2\nu)$ with a Poisson's ratio ν=0,45 The details of the experimental procedures are given elsewhere (1).

EXPERIMENTAL RESULTS

Figure 1 shows a typical record of the thickness variations of a sample before and during the explosive decompression test. Zone 2 is related to the thermal expansion of the sample during the temperature rise. Then gas under pressure is introduced into the cell. The sample thickness increases: the compressibility effect is lower than the expansion of the material by the dissolved methane. Decompression starts at the beginning of zone 4. The temperature decreases, and thermal contraction can be seen in the material. Several phenomena have to be considered:

-External pressure decreases so the material tends to increase in thickness.

-Gas near the surface diffuses out of the sample so the material near the surface tends to retract while the gas concentration is still high in the core. At this step, tensile stresses parallel to the surface are expected at the skin of the sample and compressive ones in the core. Both the kinetics of gas diffusion and external pressure drop influences the level of these stresses. When the sum of these stresses is higher than the material's mechanical strength, defects have to appear. The volume sharply increases due to gas accumulation inside the defects in the zone 5 of the LVDT curve. At the end of zone 5, the defects still appear but successively reach the surface, and gas escapes, so erratic increases and decreases of the thickness are observed in zone 6.

Figure 2 shows two kind of damage obtained during the tests: cracks and bubbles can be observed in the samples. The higher gas decompression rates show that, cracks (blisters) are observed within the samples with a maximum in the core and a main orientation parallel to the skin (fig.2a). When the decompression duration increases, bubbles appears in the core of the samples (fig.2b). For either lower decompression rates or low temperature, the samples were not damaged. The most probable origin seems to be the deformation of the sample surface which induces stresses in the core of the sample after gas desorption. These stresses can be relaxed by the formation of cracks and bubbles that are observed in some cases a long time after the decompression phase is finished.

BASIS FOR THE MODELLING

Our aim is to determine the stress field in parallelepipedic samples of polyethylene (see fig.2) by using numerical simulation based on a finite element method (FEM) in order to correlate the stress field to the damage observed. As the basic phenomena are clearly identified, the model has to integrate the variations of hydrostatic pressure, gas concentration inside the material and temperature during the tests. We have used the Abaqus code to estimate both stresses and strains in the samples during the tests. As a first approach and to simplify the problem, the following strong assumptions were made:

-Temperatures are constant in the samples. We estimate that the thermal diffusivity of these thermoplastic polymers are low enough.

-The mechanical behaviour of the samples is described by an elastic model. The investigations of Rodgers (2) show that the gas concentration can not act as a plasticizer, but we have to consider a linear increasing effect on the bulk modulus.

With these assumptions, the remaining effects can be described by simple mathematical models.

-From the geometry of the sample and the diffusion, solubility and permeability coefficients, it is possible to calculate the evolution of the gas concentration inside the sample using the Fick's laws. Table 1 gives the values of the coefficients needed for the calculations.

The hydrostatic pressure during decompression can be described by an exponential law with the form $P(t)=P(0)\exp(-B\,t)$

P(0): initial external gas pressure; t: time in second; B is an adjustable parameter for fitting the experimental decrease of the pressure.

The mechanical behaviour of the polyethylene is described by an elastic model. Young's modulus is known either from PVT experiments under hydrostatic pressure or by tensile tests at atmospheric conditions. As it is sensitive to the gas concentration, we should make it vary. In this first approach, we consider that the modulus can vary with the gas concentration estimated at each point of the mesh using the Henry's law. This is a coupling effect that we take into account by varying the modulus. For example, at 70°C, from 500 MPa under pressure to 62 MPa at atmospheric conditions, with both moduli measured, the relation between the modulus and the internal pressure P_{int} is considered to be linear:

$$E(P_{int}, 70°C)=62+P_{int}*((550-62)/10)$$

Both sorption-compression and desorption-decompression phases were modeled. The mesh is made of 2D plane strain 8-nodes quadratic elements.

Sorption-compression. The problem was to correlate the gas concentration in the polymer with the swelling effect. The compressibility of the material under hydrostatic pressure and his expansion by gas absorption are both involved in zone 3 of the curve shown in figure 1. As the orders of magnitude of the mechanical parameters are obtained by methods previously described, we can estimate the swelling of the polymer by gas under pressure as the difference between the LVDT overall measurement minus the calculated compression of the material under the hydrostatic pressure. So we calculate an expansion coefficient allowing us to describe the swelling due to the sorbed gas. The values of this coefficient are:

$6.15\ 10^{-4}\ MPa^{-1}$ at 40°C. and $1.24\ 10^{-3}\ MPa^{-1}$ at 70°C.

Desorption-decompression phase. The simulation of the desorption-decompression phase was made from the thermo-mechanical calculations using the sorption-compression results. It gives us the stresses in the material during desorption.

DISCUSSION

The calculated results discussed below are compared with two kind of decompression tests: with and without damage as follows.

Initial pressure: 10 Mpa; decompression duration: 600 s; test temperatures: at 40°C, the samples were not damaged; at 70°C, the samples present cracks (blisters) in the core with a main orientation parallel to the skin.

A comparison of the three main stresses given by FEM calculations shows that the maximum principal stress is parallel to the skin of samples. If the crack initiation is governed by this maximum principal stress, the cracks would open perpendicularly to the skin of samples, which is never the case. So, another rupture criterion has to be considered. On the other hand, the Von Mises stress is maximum in the core of the sample and decreases near the surface. In the simulation for tests at 70°C, we find that the Von Mises stress's maximum value is higher than the yield stress (5.2 MPa). At 40°C the Von Mises stresses are lower than this value. This could explain shearing and rupture of the material in the center of the samples at 70°C following the directions given by the classification of the principal stresses. A possible interpretation could be that when the yield stress is surpassed, the material creep and sites for propagation of defects might be created by the irreversible shear deformation. We think at the moment that the initiation of defects, and not their propagation, by the stresses applied is the critical phase. Our job is now to test this criterion in order to predict the explosive decompression conditions of different specimen geometries. The first results dealing with experiment-simulation comparisons are encouraging, and we will try to extend this model to other experimentally tested thermoplastic materials used for the sheathing of flexible pipelines.

CONCLUSIONS

The overall model described here is a first development of a local approach to the low density polyethylene blistering behaviour. The Von Mises equivalent stress is the main mechanical parameter which control the iniation of the blistering. To simulate the experimental results, the gas concentration can not act as a plasticizer, but we have to consider a linear increasing effect on the bulk modulus.

REFERENCES

(1).Gaillard-Devaux, E., Ph. D. Thesis, Rupture du polyéthylène en température par décompression de méthane, Ecole des Mines de Paris, 1995.
(2) Rodgers, P., Journal of Applied Science, vol.50, 1993,p.2075.

Table 1 - Permeability, diffusivity and solubility of methane throught low density polyethylene.

Temperature	Permeability (cm^3 STP cm cm^{-2} s^{-1} bar^{-1})	Diffusivity (cm^2 / s)	Solubility (cm^3 STP / cm^3 bar^{-1})
70°C	4,82 10^{-8}	4,7 10^{-7}	0,102
40°C	2,11 10^{-7}	1,66 10^{-6}	0,127

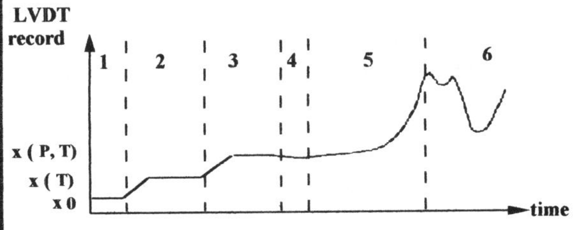
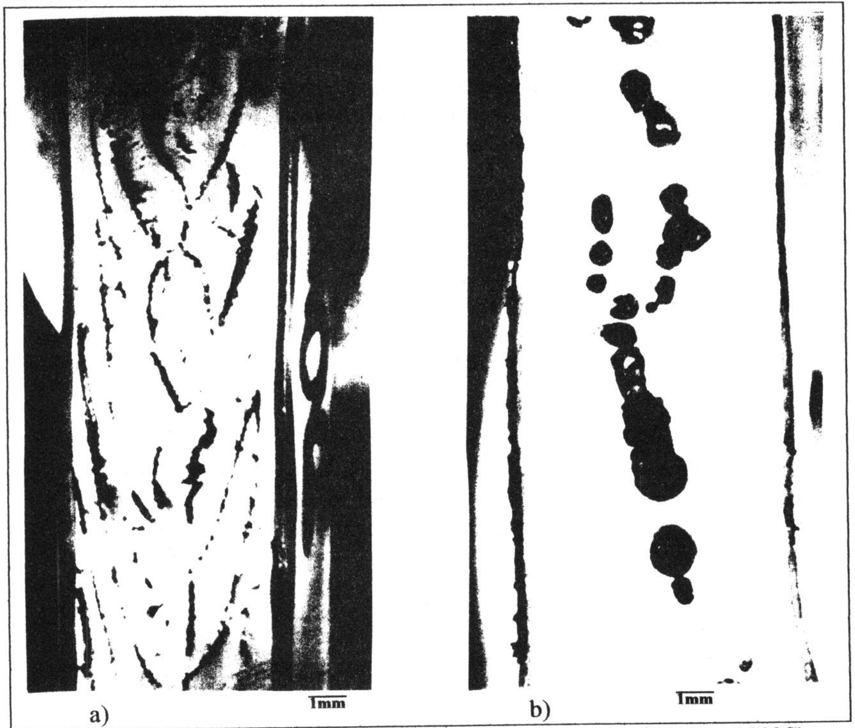


figure 1: typical record by the LVDT captor during a blistering test



a) b)

Fig. 2 Damage obtained during explosive decompression tests (10MPa; 100°C)
a) 1 minute decompression: cracks b) 1 hour decompression: bubbles.