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TEMPERATURE AND AGEING SENSITIVITY ANALYSIS OF A POLYAMIDE USED AS PRESSURE SHEATH MATERIAL IN OFFSHORE FLEXIBLE PIPES

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Abstract. *In the construction of a flexible pipe, an inner polymeric pressure sheath is the only layer which seals the conveyed fluid within the pipe structure. Therefore, understanding the mechanical behaviour of this polymer material is crucial to safe and reliable operation. Polyamide is a commonly used pressure sheath material, other options being polyvinylidene fluoride and polyethylene. One major aging mode of polyamide is the decrease in molecular weight due to the hydrolysis of the macromolecular chain. The molecular weight can be measured by the solution viscosity (CIV - The Corrected Inherent Viscosity value is an index of the molecular weight of the polyamide matrix) and this gives a very simple way to monitor the material ageing. The present work is concerned with the thermo-mechanical analysis of a particular Polyamide. The main focus is to analyse the influence of temperature and ageing in its mechanical behaviour and fracture. Fracture and tensile tests were performed over a wide range of temperatures (from -5ºC to 90°C) and corrected inherent viscosity (1.0 to 1.8 dl/g). For higher values of the CIV, the material presents a superplastic behaviour, but the behaviour tends to be brittle for lower values of the inherent viscosity and temperatures. It is proposed a general model for the uniaxial behaviour (valid for a wide range of temperatures and inherent viscosities) and also for the fracture behaviour Experiments are compared with the model predictions and show a good agreement.*

Keywords: Polyamide, Ageing, Temperature, Mechanical properties, Modelling

1. INTRODUCTION

The present paper is concerned with the modelling of the mechanical behaviour of a particular Polyamide (nylon) in tensile tests and in three-point bend fracture tests. This polyamide is often used as pressure sheaths in offshore flexible pipes. Many studies have been performed about polyamide 11 (PA-11), which has been used for 30 years in the field of oil & gas applications (Demanze et al, 2001, API 17TR2, 2003, Hochstetter et al, 2007, Hochstetter and Dang, 2009a, 2009, Berger et al 2011) and only a few about alternative materials such as Polyvinylidene fluoride (PVDF, Reis et al, for instance) and other types of Polyamides. Only a few studies about the effect of temperature and ageing in the mechanical behaviour of polyamides have been published so far.

The durability of this material is one of the reasons for using it in severe environmental conditions (temperature, high pressure, acid and hydrocarbon environment). The pressure sheaths of offshore flexible pipes can range from very low temperatures to very high ones (in the present study from -5 ºC to 90 ºC). One important limitation is the decrease of its mechanical properties due to hydrolysis. This ageing can be monitored by the decrease of the molecular weight, or Corrected Inherent Viscosity (CIV, see API 17TR2 – in the present study ranging from 1.0 dl/g to 1.8 dl/g).

The focus of the paper is to analyse the mechanical behaviour in a tensile test within a range of temperatures and Corrected Inherent Viscosities, see API 17TR2 (most of the papers concerning Polyamides are concerned on chemical aspects) and to propose model equations with material constants that can be identified with a minimum set of laboratory tests.The tensile tests show a superplastic behaviour (large deformation without a necking) even at low temperatures for a Corrected Inherent Viscosity higher that 1.2 dl/g. Besides, the rate dependency for this particular Polyamide is negligible within the range of strain rates used in the tests. The behaviour became brittle for lower values of the Corrected Inherent Viscosity (CIV<1.1 dl/g) and lower temperatures. In these cases, classical concepts of Linear Elastic Fracture Mechanics can be applied.

2. MATERIAL AND METHODS

Single-edge-cracked three-point bend fatigue specimens and tensile specimens were machined following ASTM D-638-08 and ASTM – D 5045 standards (see Fig. 1). The specimens, initially with a Corrected Inherent Viscosity $\approx$ 1.8 dl/g, are aged in autoclaves at 140°C (different number of days to obtain different values of Corrected Inherent Viscosity) in pure water with a neutral pH and with a level of residual O2 content in the ppb range. Mechanical tests were performed after ageing. The specimens were machined before ageing except for the cracks (razor blade made), which were done after ageing. The tensile tests were performed considering three different values of the Corrected Inherent Viscosity (1.04 dl/g, 1.18 dl/g and 1.8 dl/g). For a CIV = 1.8 dl/g the tests were performed at five different temperatures (0°C, 23°C, 50°C and 90°C) and for 1.18 dl/g and 1.04 dl/g, three temperatures were considered (-5°C, 23°C and 90°C). All tensile tests were performed at three different stroke velocities (0.5 mm/min, 5 mm/s and 50 mm/s). The fracture tests with constant velocity (v=10 mm/min) were performed at three different temperatures (-5 ºC, 23 ºC, 90 ºC) and three different values of Corrected Inherent Viscosity (1.02 dl/g, 1.3 dl/g and 1.05 dl/g).

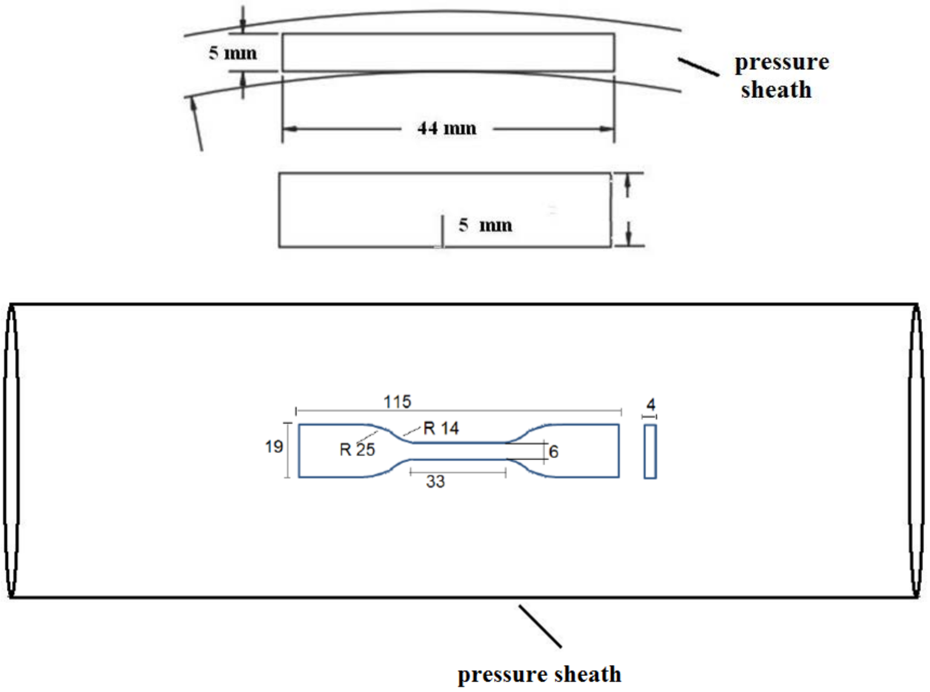

Figure 1. Single-edge-cracked three-point bend fatigue specimens and tensile specimens fabricated from a pressure sheath taken from a flexible pipe.

3. RESULTS AND DISCUSSION

3.1. Three-point bend tests

A superplastic behaviour is observed for higher values of the temperature and of the Corrected Inherent Viscosity (see Figs. 2 and 3). The behaviour became brittle for lower values of the Corrected Inherent Viscosity (CIV<1.1 dl/g) and lower temperatures ($\theta \leq 25$ ºC). In these cases, classical concepts of Linear Elastic Fracture Mechanics can be applied.

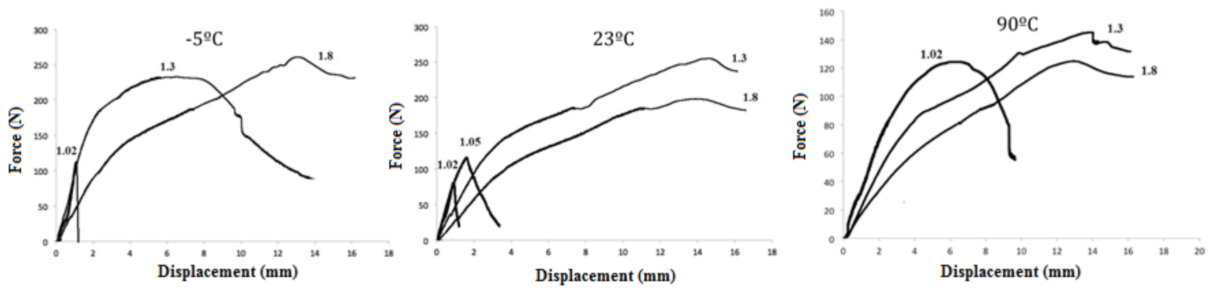

Figure 2. Three-point bending tests at different temperatures and CIV´s.

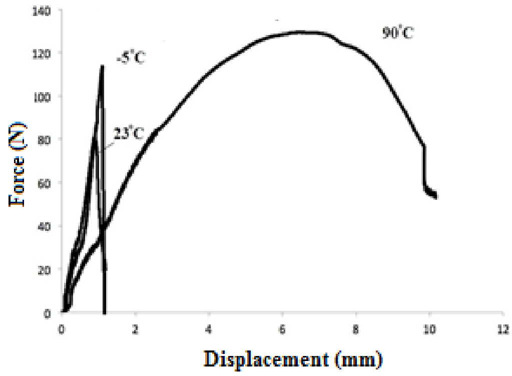

Figure 3. Three-point bending test with a CIV = 1.02 dl/g and three different temperatures.

As it can be observed in Fig. 4, for a CIV>1.1 and above 23ºC, the behaviour is superplastic and the crack propagation is negligible.

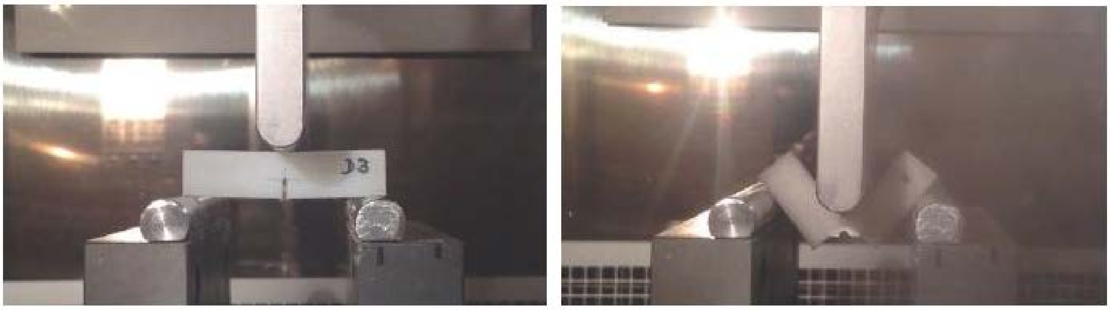

Figure 4. Typical fracture test with CIV > 1.1.

3.2. Tensile tests

3.2.1. Preliminary definitions

The classical uniaxial engineering stress and engineering strain will be noted, respectively, σ and ε

$$\sigma = \frac{F(t)}{A_0} \quad ; \quad \varepsilon(t) = \frac{\Delta l(t)}{l_0} \tag{1}$$

$F(t)$ is the axial force necessary to impose an elongation $\Delta l(t)$ at a given instant t. l_0 is the gauge length and A_0 the cross-section area. In the analysis, it is interesting to use the logarithmic measure of strain ε_t and to use an auxiliary variable σ_t defined as follows

$$\sigma_t = \sigma(1+\varepsilon) \quad ; \quad \varepsilon_t = \ln(1+\varepsilon) \tag{2}$$

In the case of specimens with negligible volume change, σ_t is usually called the "true stress". It is important to observe that, although this change of variables is quite useful (to use σ_t in the place of σ making the resulting mathematical expressions more compact), such a denomination is not adequate in the present case, since the volume do not necessarily remain constant. Nevertheless, to keep the traditional nomenclature, from now on the auxiliary variable σ_t will be called true stress and ε_t the true strain. Tests were performed with constant strain rate, ranging from 0.5 mm/s to 50 mm/s. One amazing feature of this polyamide is that the rate dependency is negligible with the stroke velocity between 0.5 mm/min and 50 mm/s. Within this range of strain rates, the material behaviour is rather elasto-plastic than elasto-viscoplastic. Fig. 5 and 6 present the stress-strain curves for three different stroke velocities, respectively at 23 ºC and 90 ºC.

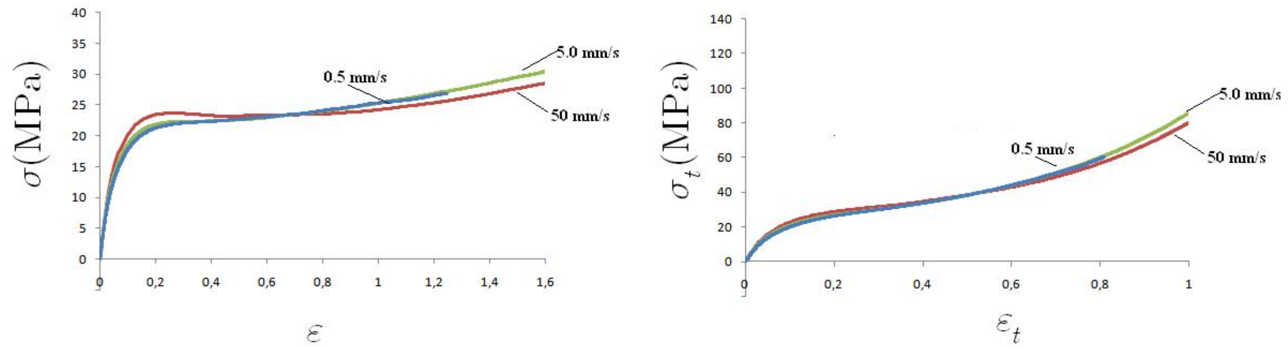

Figure 5. Stress-strain curves at 23ºC with different strain rates. CIV = 1.8 dl/g.

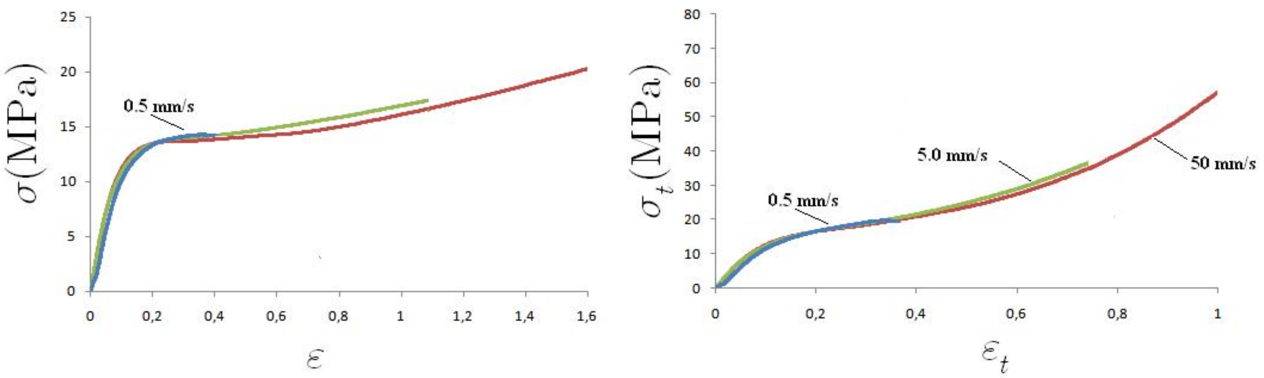

Figure 6: Stress-strain curves at 90ºC with different strain rates. CIV = 1.8 dl/g.

3.2.2. Modelling the superplastic behaviour of the polyamide

In this section, a model is proposed for tensile tests of this particular polyamide, with a CIV=1.8 dl/g at different temperatures. The main features of the models for both monotonic and cyclic behaviour are very similar to the proposed in Nunes et al, 2011a, Nunes et al 2011b and da Costa Mattos and Martins, 2013. The model is divided in two parts: the first one that is more adequate for $\left(\partial^2\sigma_t \; / \; \partial\varepsilon_t^2\right) \le 0$ and a second one, that is more adequate for $(\partial^2\sigma_t \; / \; \partial\varepsilon_t^2) > 0$. The strain $\varepsilon *$ characterize the transition: $(\partial^2\sigma \; / \; \partial\varepsilon^2) \le 0$ to $(\partial^2\sigma \; / \; \partial\varepsilon^2) > 0$. The following equations are proposed:

$$\sigma_t = v_1(1 - \exp(-v_2\varepsilon_t)) \text{ if } \varepsilon_t \le \varepsilon * \quad ; \quad \sigma_t = a + k(\varepsilon_t)^n \text{ if } \varepsilon_t > \varepsilon * \tag{3}$$

v_1 , v_2, a , k and n are temperature dependent material parameters that characterize the material, defined as follows:

$$\varepsilon^* = 0.2\,;\; v_1 = -0.149\;\theta + 32.16\,;\; v_2 = -0.072\;\theta{+}17.12 \tag{4.1}$$

$$a = -0.161\;\theta{+}31.47\,;\; k = -0.295\;\theta{+}66.23\,;\; n = 2.55 \tag{4.2}$$

The experimental curve and model prediction for different temperatures are presented in Fig. 7

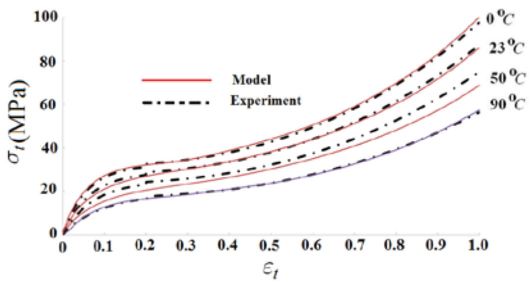

Figure 7. Stress-strain curves obtained at 0ºC, 23ºC, 50ºC e 90ºC. VIC = 1.8 dl/g.

3.2.3. Modelling the coupling between ageing and temperature

In order to analyse the coupling between ageing and temperature, tensile test were performed at three different values of the Corrected Inherent Viscosity (1.04 dl/g, 1.18 dl/g and 1.8 dl/g) and four different temperatures (0°C, 23°C, 50°C and 90°C). The following values of ε^* have been identified: ε^*= 0.2 for a CIV = 1.8dl/g; ε^*= 0.14 for a CIV = 1.18 dl/g and ε^* = 0.10 for a CIV = 1.04 dl/g. In practical applications, the maximum strain is limited between 2% to 5%. The following model coupling ageing and temperature is proposed for smaller values of the deformation

$$\sigma_t = v_1(1 - \exp(-v_2\varepsilon_t)) \tag{5}$$

with

$$v_1 = -a_1\ \theta + a_2$$
$$a_1 = -\alpha_1 + \beta_1\ CIV - \gamma_1\ CIV^2$$
$$a_2 = \alpha_2 - \beta_2\ CIV$$
$$v_2 = -b_1\ \theta + b_2$$
$$b_1 = (-\eta_1 + \lambda_1\ CIV - \delta_1\ CIV^2)^{-1}$$
$$b_2 = (-\eta_2 + \lambda_2\ CIV - \delta_2\ CIV^2)^{-1}$$

Table 1 depicts the material constants identified experimentally for this material. Only six tests (two temperatures and three values of CIV) are necessary to characterize the material behaviour.

Table 1: Material constants (eq. (5))

α_1	β_1	γ_1	α_2	β_2	η_1	λ_1	δ_1	η_2	λ_2	δ_2
1.01	1.96	72.70	82.07	27.84	251.57	372.80	130.90	28.21	45.10	14.53

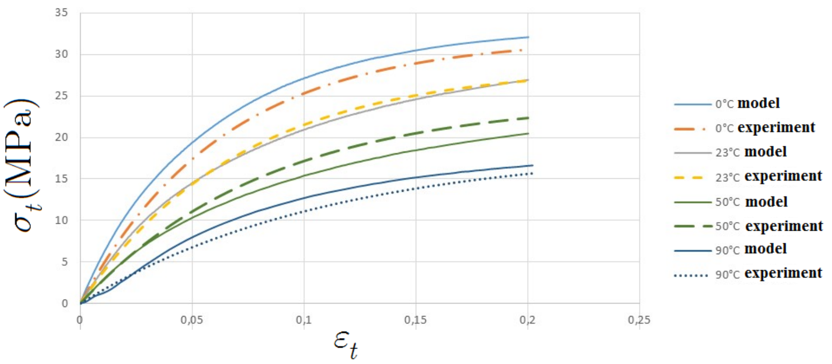

Figure 8. True stress X true strain curves comparison between experiments and model predictions. CIV = 1.8 dl/g.

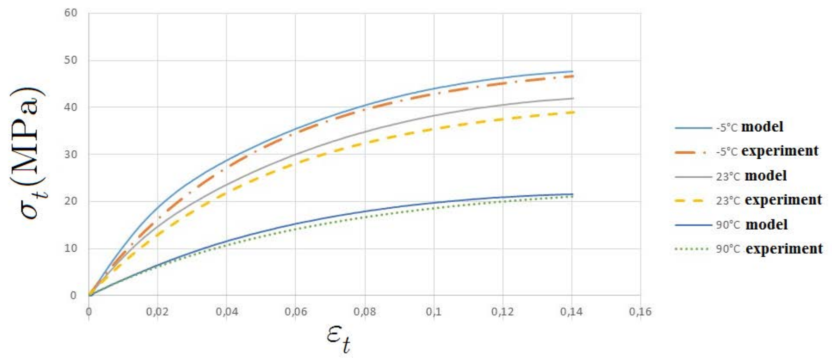

Figure 9. True stress X true strain curves comparison between experiments and model predictions. CIV = 1.18 dl/g.

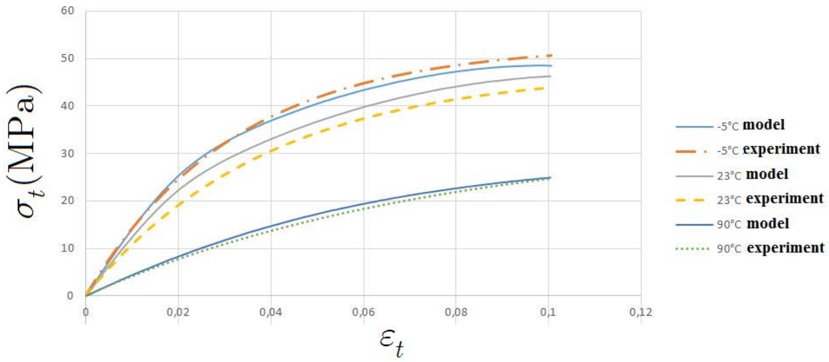

Figure 10. True stress X true strain curves comparison between experiments and model predictions. CIV = 1.04 dl/g.

4. CONCLUSIONS

The present paper is concerned with the analysis of the effect of ageing and temperature on the tensile behaviour of a particular type of polyamide in tensile tests and in three-point bend fracture tests. One major aging mode is the decrease in molecular weight due to the hydrolysis of the macromolecular chain. The molecular weight can be measured by the solution viscosity and this gives a very simple way to monitor the material ageing. It was verified that this polymer has a superplastic behaviour above room temperature for a range of Corrected Inherent Viscosity until 1.8 dl/g) but a brittle behaviour for a CIV<1.1 dl/g and bellow room temperature. Therefore, a good criteria to avoid crack propagation is to limit the Corrected Inherent Viscosity do a value above 1.1 dl/g. Another interesting feature is that this particular Polyamide does not present a significant rate dependency in the range of loading rates adopted in the present study. Models were proposed for simulating tensile test under different temperatures and Corrected Inherent Viscosity, showing an adequate correlation with experimental results.

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