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Modelling of thermal ageing effect on elastic-viscoplastic behaviour of semi-crystalline polymers by D.N.L.R approach

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Abstract

This work is devoted to the numerical and experimental study of thermal ageing effect on microstructure and mechanical properties of HDPE. Uniaxial tension tests were conducted at 25 °C in order to characterize the large deformation response of HDPE. The influence of thermal ageing on the alteration of the large deformation response of HDPE was examined. A Distribution of Non Linear Relaxation (D.N.L.R) Approach was used to describe the mechanical response of virgin HDPE. The thermal ageing effect was incorporated into the constitutive model to capture the stress-strain behaviour up to failure of aged HDPE. The model is shown to be in good agreement with experimental results.

Keywords: ageing thermal, HDPE, finite strain, D.N.L.R. approach

1. Introduction

In a practical field, polymer materials have been shown to express some advantages, for instance, light-weight, high-strength, anti-rust, and easily processable. These advantages were based on the comparison with metal and inorganic materials.

Actually, the specific strength of polymer materials is relatively high and polymer materials do not form the colored rust like metal. However, polymer materials degrade under various circumstances such as low and/or high temperature, exposure to rain and/or sunlight, under the water and/or soil. Polymer materials are applicable for various purposes, for example, reduction of weight, vibration isolating and damping, coating and covering, and heat insulation. Some products are applicable to interior and exterior parts of automobile, railway vehicle, air plane, and ship. Some products are also applicable to buildings, houses, construction, commodities, house wares, pipelines for transportation of potable and waste water, electrical appliances, and toys. Through respective service life, various properties of polymer materials were changed by the degradation, for example, oxidation, hydrolysis, ultra-violet

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(UV) irradiation, chemicals influence, ageing, fatigue, swelling, wet and dry cycle, and complex condition of respective degradation [1-3].

1.1. Scope of this work

The present work is aimed at modelling the effect of thermal ageing on the elastic viscoplastic behaviour of semi crystalline HDPE. Our goal is to understand the mechanisms that cause the ageing of HDPE, and the resulting effects on its mechanical behaviour. The influence of ageing thermal on the PE100 is examined by the Fourier transform infrared spectroscopy (FTIR) and static mechanical measurements. A robust constitutive model able to capture the finite strain behaviour of polymers is essential to predict the thermal ageing effect on the overall stress–strain response. Various models were developed to describe the large elastic–viscoplastic deformation of polymers: Cunnat et al [4-5]; Boyce et al. [6-7]; Arruda et al.[8]; Buckley and Jones [9]; Wu and van der Giessen [10]; Bardenhagen et al. [11]; Tervoort et al. [12]; Adams et al. [13]; Ahzi et al [14]; Dupaix and Krishnan [15]; Ayoub et al. [16]; Arieby., [17]; M'rabet.[18], among many other references). In the present work, a D.N.L.R approach based on the generalization of Gibbs relationship for the outside equilibrium systems and the use of the fluctuation theory to analyze the material dissipation due to its internal reorganization was selected and modified to include the thermal ageing effect.

The paper is organized as follows. Section 2 is focused on the experimental investigations that were conducted on semi crystalline HDPE. Section 3 introduces the main features of the constitutive model. The methodology for the calibration of the model parameters is detailed and model results are compared to experimental data. Finally, concluding remarks are given in Section 4.

2.1 Material and methods

2.1.1 Initial characteristics of material

The HDPE material used in this study is a PE100. Made in a first time as granules, imported by the CHIALI enterprise situated in SIDI BELABES (Algeria). He was then extruding in order to manufacture tubes of different diameters. It is about a semi-crystalline thermoplastic, including an amorphous phase and a crystalline phase presenting themselves as an aggregation sphérolitique.

His molar mass is the order of 500 g/mol, the fusion and glass transition temperatures are respectively 135 °C and -125 °C.

2.1.2 Thermal ageing methods

PE 100 tubes were cut into rectangular shaped samples of dimension 100x15x 6 mm³.we put these samples inside the steam room under the following conditions:

- Speed of heating is of 5°C/Mn
- maintenance during different lengths 48h, 96h, 144h, 192h at 90 °C
- cooling in the steam room.

2.1.3 Mechanical analysis

The stress- strain behavior of HDPE before and after thermal ageing effect was characterized under uniaxial tension on an electromechanical testing machine. The local strain was measured using a video-controlled system (VideoTraction) consisting of a CCD camera interfaced with a computer. One of the main advantages of the VideoTraction method is its ability to keep the local true strain-rate constant (G'Sell et al.,2002). This technique is based on the follow-up of 4 markers printed on the front surface of the sample, where two among them are aligned along the tensile direction and the two other according to the transverse direction. The data acquisition system automatically records the true stress versus the true strain, using the initial sample dimensions and assuming incompressibility. The experiments were achieved at the same temperature but under a single local true strain rate of 10⁻³ s⁻¹.

2.2 Experimental results

2.2.1 Effect of thermal ageing on the mechanical behavior

For the evolution of the true stress, three domains of deformations can be distinguished. At the beginning, the material shows an elastic expansion related to Poisson's ratio of the material, which is followed by a slight contraction when the material enters the plastic domain near the yield stress, during stretching, plastic compaction (contracting volume strain for intermediate stretching ratio) is in competition with dilatation in the control of volume change. The compaction phenomenon is magnified, for which the mobility of the amorphous chains and the time to accommodate macroscopic deformation are favoured. In higher strains, the final hardening stage, during which microstructural rearrangements and orientation mechanisms gradually occur in HDPE. During this final stage, homogenous stretching or local necking occur with visible whitening of the samples, resulting from the crazes formation in the amorphous layers between crystalline lamellae and causing important dilatation of polymers under tension (figure 1). Large dilatation is partly due to the transformation of the initial spherulitic order into fiber-type morphology, and partly to cavitations process in the material.

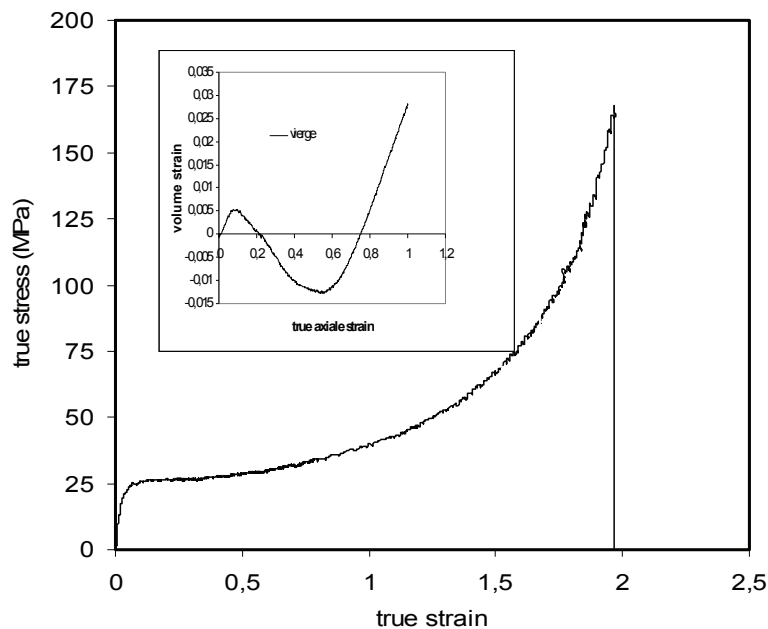


Fig.1: Mechanical behaviour of virgin PE100 (true axial stress - true axial strain)

The stress – strain curves of HDPE stretched up to failure before and after thermal ageing is shown in Fig. 2. Most of the tensile properties of HDPE are affected by thermal ageing. Indeed, significant changes in elastic modulus, yield stress and strain at break are highlighted. More precisely and as clearly shown in Fig. 2, yield stress and stress at break increase with ageing thermal. One can observe a drop of the yield stress from its initial value of 24 MPa before ageing to a value of 42MPa after ageing a during 96h at 90°C. The stress at break increases from 150 to 300 MPa. The yield stress of polymer is related to its intermolecular interactions between neighbouring polymer chain segments. Indeed, the intermolecular interactions represent the main physical parameter determining the mechanical response at low strains.

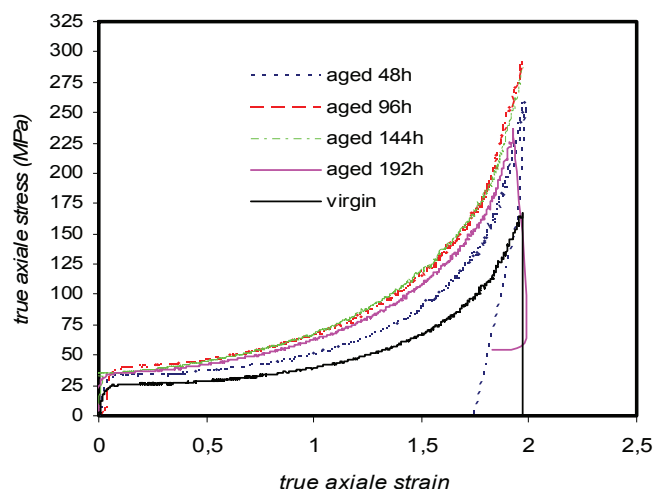


Fig.2: Thermal ageing effect on mechanical behaviour of PE100 (true axial stress - true axial strain)

This increase of the yield stress is explained by an increase of the rate of crystallinity, the phenomenon is called post-crystallization. Then a reduction of these limits with the increase of the length of the ageing, that stabilizes from 144h and 192h ageing.

2.2.2. Microstructure characterization by Fourier Transform Infrared Spectroscopy (FTIR)

In order to reveal all the chemical modifications that can be at the origin of this result, the FTIR confirmed well that no supplementary chemical link is produced (Fig.3). One notes that the intensity of the peaks of transmittance of the C=C links and C-H are not influenced by the length of the ageing thermal, it remains nearly unaltered, what confirms that the change of the mechanical behavior of the PEHD, is not due to the modification of the present chemical groups in the material, but to the phenomenon of structural morphology change that one designated by post-crystallization.

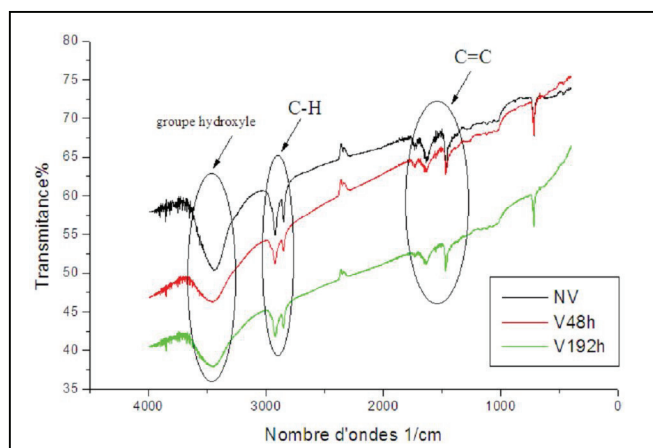


Fig.3: Superposition of the FTIR specters of the samples (virgin, aged 48h, aged 192h)

3. Modeling

In the first part of this section, we present the D.N.L.R. approach (Cunat. 1988) before ageing. In the second part, we present the modifications which were introduced to include the effect of thermal ageing. In the last part, the simulated stress–strain responses are compared to the experimental results.

3.1 D.N.L.R Approach

In the field of mechanical engineering, the constitutive equations of the DNLR approach are:

$$\underline{\underline{\sigma}} = \sum_j \underline{\underline{\sigma}}^j = \sum_j P_0^j \underline{\underline{a}}^u \underline{\underline{\varepsilon}} - \frac{\underline{\underline{\sigma}}^j - \underline{\underline{\sigma}}^{j,r}}{\tau^{j,r}} \tag{1}$$

$$\underline{\underline{\sigma}} = \sum_j \underline{\underline{\sigma}}^j = \sum_j P_0^j \underline{\underline{a}}^u \underline{\underline{\varepsilon}} - \frac{\underline{\underline{\sigma}}^j - \underline{\underline{\sigma}}^{j,r}}{\tau^{j,r}} \tag{2}$$

Where $\underline{\underline{\sigma}}$ and $\underline{\underline{\varepsilon}}$ are respectively stress and strain tensors, $\underline{\underline{a}}^u$ and $\underline{\underline{a}}^r$ are respectively the elastic and relaxed modulus, $\underline{\underline{\sigma}}^r$ and $\underline{\underline{\sigma}}^{equil}$ is the relaxed and equilibrium stress tensor. The global response of the material is the sum of each modal stress represented by $\underline{\underline{\sigma}}^j$. The weight P_0^j of each mode is obtained by an extension of the fluctuation theory which leads to:

$$P_0^j = \frac{\sqrt{\tau^{j,r}}}{\sum_j \sqrt{\tau^{j,r}}} \tag{3}$$

Where $\tau^{j,r}$ is the relaxation time of the j^{th} mode.

In case of uniaxiale tensile we introduce the effective elastic modulus to describe damaging, the constitutive equations are:

$$\underline{\underline{\sigma}}_1 = \sum_{j=1}^N \underline{\underline{\sigma}}_1^j = E^{eff} \underline{\underline{\varepsilon}}_1 - \sum_{j=1}^N \frac{\underline{\underline{\sigma}}_1^j - P_j^r \underline{\underline{\sigma}}_1^{j,r}}{\tau_j^r} \tag{4}$$

$$\underline{\underline{\sigma}}_1^r = \sum_{j=1}^N \underline{\underline{\sigma}}_1^{j,r} = E^{eff,r} \underline{\underline{\varepsilon}}_1 - \sum_{j=1}^N \frac{\underline{\underline{\sigma}}_1^{j,r} - P_j^{eq} \underline{\underline{\sigma}}_1^{j,eq}}{\tau_j^{eq}} \tag{5}$$

For modelling the elasticity modulus versus of the axial strain, we recourse to the following empiric law:

$$E^{r,eff} = E^r \left[1 - \left[\alpha_1 (1 - \exp(-\beta_1 \varepsilon_1)) - \frac{1}{5} X \ell^{-1} (\lambda_c / n^{0.5}) \varepsilon_1 \right] \right] \tag{6}$$

$$E^{eff} = E \left[1 - \left[\alpha_1 (1 - \exp(-\beta_1 \varepsilon_1)) - \frac{1}{5} X \ell^{-1} (\lambda_c / n^{0.5}) \varepsilon_1 \right] \right] \tag{7}$$

The equilibrium stress was approached by the 8- chains model of Arruda and Boyce [6], which is based on the statistical theory related to molecular chains.

In the case of uniaxial sollicitation (tensile-compression), this stress evolution obeys to the following expression:

$$\sigma_1^{eq} = \frac{N_{rl} K_B T}{3\lambda_c} n^{0.5} (\lambda_1^2 - \lambda_2^2) \ell^{-1} \left(\frac{\lambda_c}{n^{0.5}} \right) \quad (8)$$

$$\lambda_1 = \exp(\varepsilon_1) \quad (9)$$

$$\lambda_2 = 1/\sqrt{\lambda_1} \quad (10)$$

$$\lambda_c = \sqrt{\lambda_1^2 + \frac{2\lambda_2^2}{3}} \quad (11)$$

The model flexibility of Arruda and Boyce [7] lives in the possibility of reproducing the hardening led by stretching and reorientation of chains, in big deformations, by bringing in only two parameters n and NKT . These last ones allow finding the global shape of the hyperelastic hardening.

The corresponding good values (listed below in the table) of these parameters are gotten after several simulations.

Value of material parameters for HDPE:

E(MPa)	E ^r (MPa)	n	NKT	α_1	β_1
1180	450	90	0.53	0.899	18

3.2 Thermal ageing

The constitutive model is extended to account for the thermal ageing effect. The adopted approach does not consider all the elementary chemical mechanisms. Indeed, we only focus on the evolution of some material quantities appearing in the constitutive model.

It was previously observed that the thermal ageing strongly acts on the loss of mass in HDPE. To describe the evolution of the mechanical properties when submitted to ageing thermal, the loss of mass was taken as the representative variable of the degree of ageing. The ageing parameters defined as:

$$D = \frac{\Delta m}{m_0} = \frac{m(t) - m_0}{m_0} = \frac{m(t)}{m_0} - 1 \quad (12)$$

Where:

m_0 : The initial mass (before the ageing)

$m(t)$: Evolution of the mass according to the time of ageing

The evolutions of the elastic and relaxed modulus after the thermal ageing are given by the formulas (13) and (14):

$$E_{eff}^{r,v} = \frac{E^r}{1+D} \left[1 - \left\{ \alpha_1 (1 - \exp(-\beta_1 \varepsilon_1)) - \frac{1}{5} X \ell^{-1} \left(\frac{\lambda_c}{n^{0.5}} \right) \varepsilon_1 \right\} \right] \quad (13)$$

$$E_{eff}^v = \frac{E}{1+D} \left[1 - \left\{ \alpha_1 (1 - \exp(-\beta_1 \varepsilon_1)) - \frac{1}{5} X \ell^{-1} \left(\frac{\lambda_c}{n^{0.5}} \right) \varepsilon_1 \right\} \right] \quad (14)$$

The evolution of the true stress and the true stress relaxed after thermal ageing is given by the following formulas:

$$\sigma_1^v = \frac{E_{eff}^v}{1+D} \varepsilon_1 - \sum_{j=1}^N \frac{\sigma_1^j - P_j^r \sigma_1^{j,r}}{\tau_j^r} \quad (15)$$

$$\sigma_1^{r,V} = \frac{E^{eff,r}}{1+D} \varepsilon_1 - \sum_{j=1}^N \frac{\sigma_1^{j,r} - P_j^{eq} \sigma_1^{j,eq}}{\tau_j^{eq}} \quad (16)$$

3.3 Comparison of model and experiments

In what follows, the comparison of simulations with experimental uniaxial tensile results will be presented.

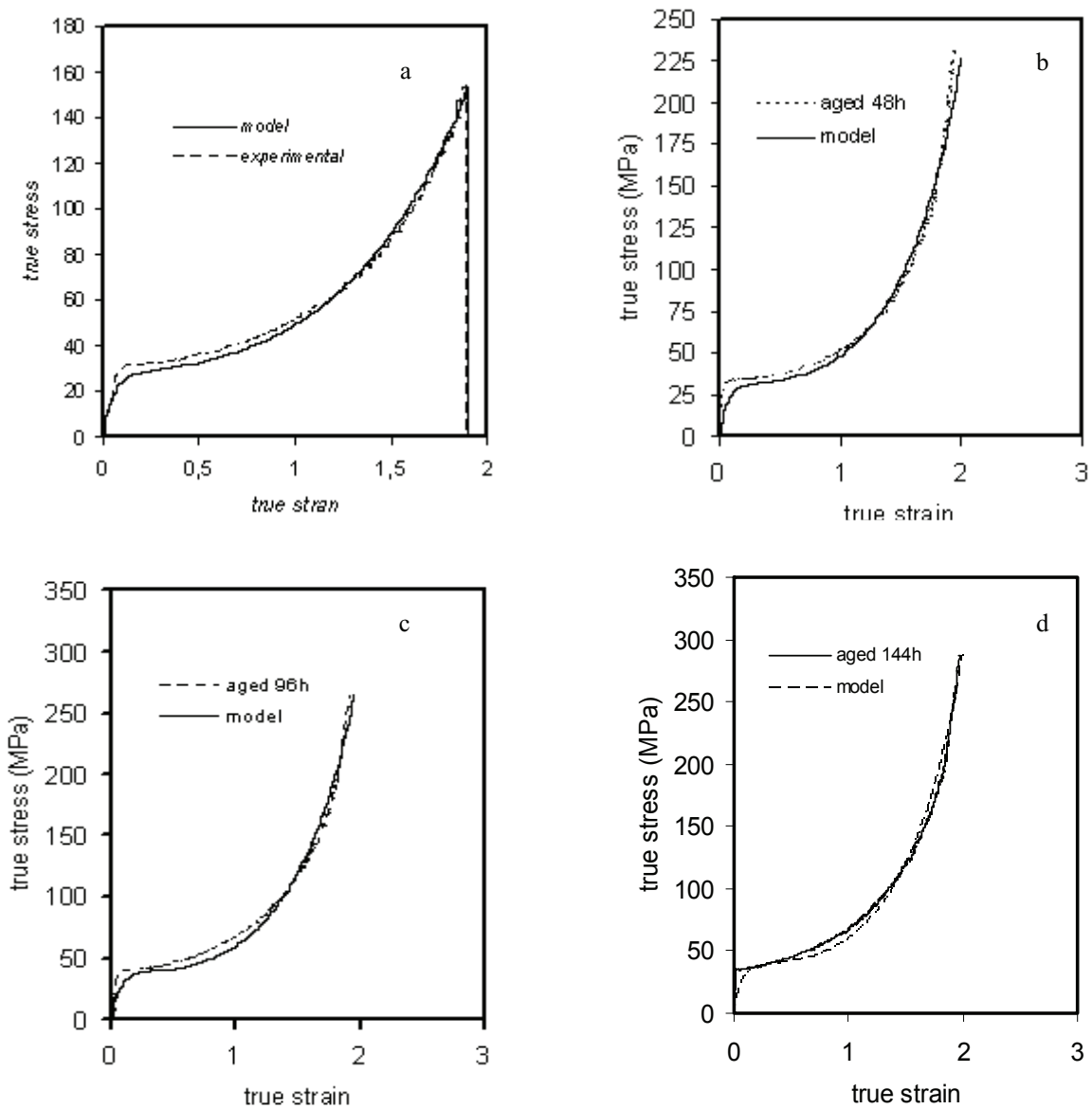


Fig.4: Comparison of simulation results (solid lines) and experimental data (dashed lines) for stress-strain behaviour of PE100 at different ageing time: (a) virgin state, (b) 48h, (c) 96h, (d) 144h.

Fig.4 shows the capability of the model to capture the stress–strain behaviour of aged PE100 at different times of thermal ageing. Indeed, it can be seen that the model is able to reproduce most of the features of the stress–strain curves: the initial stiffness, the non linear response and the hardening zone.

3. Conclusion

In this work, the thermal ageing effect on HDPE was studied. Uniaxial tensile tests were conducted to investigate the thermal ageing effect on the large deformation stress–strain behavior of PE100. The thermal ageing leads to an increase of mechanical properties. In particular, yield stress and stress at break. In order to reveal any chemical changes that may be causing this result, the IRTF has confirmed that no additional chemical bond is produced. A D.N.L.R approach based on the generalization of Gibbs relationship for the outside equilibrium systems was used to describe the mechanical response of PE100 in its virgin state. The model was extended to include the thermal ageing effect on the stress–strain relation ship of PE100. The simulations were compared to experimental results and fair agreement was found for a variety of time ageing.

References

- [1] Dobinson F, Preston J. New high - temperature polymers. II. Ordered aromatic co polyamides containing fused and multiple ring system. *J Polym Sci Part A-1* 1966; 4: 2093–105.
- [2] Hale WF, Farnham AG, Johnson RN, Clendinning RA. Poly (aryl ethers) by nucleophilic aromatic substitution. II. Thermal study. *J Polym Sci Part A-1 Polym Chem* 1967; 5: 2399–414.
- [3] Cameron GG, Kerr GP. Thermal degradation of polystyrene – I. Chain scission at low temperatures. *Eur Polym J* 1968; 4: 709–17.
- [4] Cunat C. the DNL approach and relaxation phenomena: Part I – historical account and DNL formalism. *Mech. Of time – depend. Mater.* 5, 39-65. (2001)
- [5] Cunat C. Approche statistique des propriétés thermodynamiques des états liquides et vitreux. Relaxation des liquides et transition vitreuse. Influence des associations chimiques. *These d'état, University de Nancy I.* (1985).
- [6] Boyce, M.C., Parks, D.M., Argon, A.S., Large inelastic deformation of glassy polymers. Part I: rate dependent constitutive model. *Mechanics of Materials* 7, 1988, 15–33.
- [7] Boyce, M.C., Socrate, S., Llana, P.G., Constitutive model for the finite deformation stress–strain behaviour of poly (ethylene terephthalate) above the glass transition. *Polymer* 41, 2000, 2183–2201.
- [8] Arruda, E.M., Boyce, M.C., Jayachandran, R. Effects of strain rate, temperature and thermo mechanical coupling on the finite strain deformation of glassy polymers. *Mechanics of Materials* 19, 1995, 193–212.
- [9] Buckley, C.P., Jones, D.C., 1995. Glass–rubber constitutive model for amorphous polymers near the glass transition. *Polymer* 36, 3301–3312.
- [10] Wu, P.D., van der Giessen, E., On neck propagation in amorphous glassy polymers under plane strain tension. *International Journal of Plasticity* 11, 1995, 211–235.
- [11] Bardenhagen, S.G., Stout, M.G., Gray, G.T., Three-dimensional, finite deformation, viscoplastic constitutive models for polymeric materials. *Mechanics of Materials* 25, 1997, 235–253.
- [12] Tervoort, T.A., Smit, R.J.M., Brekelmans, W.A.M., Govaert, L.E., A constitutive equation for the elasto-viscoplastic deformation of glassy polymers. *Mechanics of Time-Dependent Materials* 1, 1997, 269–291.
- [13] Adams, A.M., Buckley, C.P., Jones, D.P., Biaxial hot drawing of poly(ethylene terephthalate): measurements and modelling of strain-stiffening. *Polymer* 41, 2000, 771–786.
- [14] Ahzi, S., Makradi, A., Gregory, R.V., Edie, D.D., Modeling of deformation behavior and strain-induced crystallization in poly(ethylene terephthalate) above the glass transition temperature. *Mechanics of Materials* 35, 2003, 1139–1148.
- [15] Anand, L., Gurtin, M.E., A theory of amorphous solids undergoing large deformations, with application to polymeric glasses. *International Journal of Solids and Structures* 40, 2003, 1465–1487.
- [16] Makradi, A., Ahzi, S., Gregory, R.V., Edie, D.D., A two-phase self-consistent model for the deformation and phase transformation behavior of polymers above the glass transition temperature: application to PET. *International Journal of Plasticity* 21, 2005, 741–758.
- [17] Ayoub, G., Zarri, F., Naït-Abdelaziz, M., Gloaguen, J.M., Modelling large deformation behaviour under loading–unloading of semi crystalline epolymers: application to a high density polyethylene. *International Journal of Plasticity*, in press, 2009.
- [18] M'Rabet .K, Rahouadj R., Cunat C. Modélisation thermodynamique multiéchelle du comportement élasto-visco-plastique du PEHD en grandes déformations uniaxiales séquences. *CFM*, 2007.