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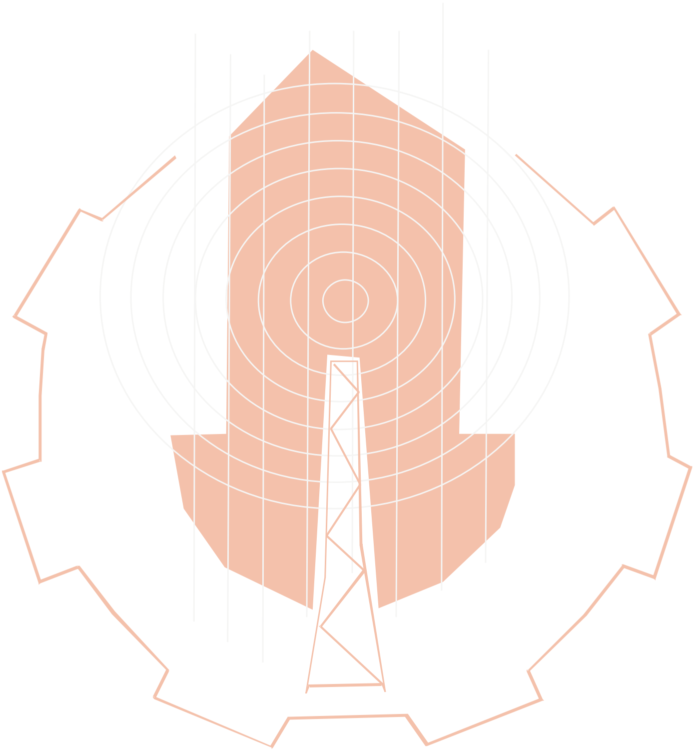

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EFFECTS OF LOADING HISTORY ON THE MECHANICAL BEHAVIOR OF SEMI-CRYSTALLINE POLYMER

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الملخص

يقدم البحث دراسة عملية للسلوك الميكانيكي خلال عملية التشكيل لبوليمر البولي ايثيلين العالي الكثافة (HDPE)، اخذين في الاعتبار الانهيار الحادث نتيجة الانفعالات الكبيرة. ان الخواص الميكانيكية وآلية التشكيل تعتمد بشكل كبير على نوع القوى المطبقة وبالتالي من المهم دراسة تأثير تاريخ التحميل الناتج عن التشكيل السابق الحادث نتيجة للقوى المطبقة. ولتحديد هذا التأثير على الخصائص الميكانيكية وبشكل أدق التغير في الحجم وتطورهما خلال التشكيل تم إجراء سلسلة من التجارب المختلفة والمتضمنة عملية الشد الاحادية المحور وكذلك عمليات الشد والضغط المتعاقبة واختبار الشد الدوري عند مستويات انفعال مختلفة. تم على عينات شد مصنعة من لوح من البولي ايثيلين المبثوق. النتائج العملية بينت بوضوح أن السلوك الميكانيكي للبولي ايثيلين العالي الكثافة يتأثر بشكل كبير بمعدلات الانفعال المطبقة والمسبقة التطبيق اما فيما يتعلق بتجربتي الشد الدوري وتجربة الشد والضغط المتعاقب والمتضمنة لفترة الاستعادة فلا تعتمد على تاريخ الاحمال السابقة على كل من الاجهاد والتغير في الحجم. وبهدف التوقع ومحاكاة السلوك الميكانيكي للبوليمر بما في ذلك محاكاة التغير في الحجم تم تقديم نموذج رياضي اعتمادا على إجراء بعض التعديلات الخاصة على نموذج يستخدم علاقات رياضية في الديناميكا الحرارية والتي تهدف لدراسة السلوك اللاخطى لظاهرة الانعكاسية. النتائج النظرية المتحصل عليها من استخدام النموذج وتلك المتحصل عليها من التجارب العملية تبين مدى قدرة النموذج على محاكاة السلوك اللاخطي للبوليمر والمتغير اعتمادا على تاريخ الاحمال بشكل صحيح.

ABSTRACT

The mechanical behavior of semi-crystalline polymer has been characterized experimentally taking into account the damage occurring in large deformation. The mechanical properties and deformation mechanism are dependent on the applied loading types. Therefore, the influence of the loading history resulted from prior deformation due to the applied loading types executed are studied. To quantify this effect, samples of high density polyethylene were tested under uniaxial tension with several loading paths, monotone, loading/unloading/recovery/reloading and cyclic tests at different strain levels, even at large deformation. The volume strain was determined in real time during the tests by an optical extensometer. The results show clearly that, the mechanical behavior of High Density Polyethylene (HDPE) is significant affected by the strain rate history, but for the cycling recovery and cycling deformation tests, no history loading dependency for the stress and volume strain was found. In order to predict the damaged behavior of semi-crystalline polymer, a constitutive model was developed in which the elasto-viscoelastic-viscoplastic behavior of material and the influence of damage causing volume variation are described. A new thermodynamic potential based on a non-equilibrium thermodynamic approach of irreversible processes was introduced in the developed model. The model was validated for high density polyethylene (HDPE), which showed the ability of the model to reproduce complex loadings paths, and to predict the mechanical behavior based on loading history.

KEYWORDS: Semi-Crystalline Polymers; Cyclic Deformation; Recovery; Loading History; Volume Strain; Constitutive Equations.

INTRODUCTION

Study of deformation damage of semi-crystalline polymers is complicated due to the heterogeneity of their structure constituted by amorphous and crystalline phases. HDPE is among the most widely used polymeric solids, and it is often regarded as a model material for the study of the mechanical behavior of semi-crystalline polymers. Comparing to other semi-crystalline polymers, HDPE have the higher ductility and crystallinity at room temperature and, its yield strength and Young's modulus values are among the lowest of all the semi-crystalline polymers. The exceptional properties of HDPE making it an excellent candidate for many industrial applications, therefore experimental data for simple and complex loading paths are increasingly needed. In addition, comprehensive understanding and predicting of its mechanical behavior is extremely importance in order to make better choices in the components design and their durability.

Mechanical behavior of semi-crystalline polymers including the effects of volume change during deformation, mainly associated with the damage phenomena, has received a considerable attention in many researches. This physical phenomenon plays a very important role and provides an important additional information on the mechanical behavior, especially on the elastic properties [1,2]. Several experimental studies have been developed on a wide range of polymers to characterize the complex nonlinear behavior and volume strain depending on various external factors, such as strain rate, temperature, thermal aging, and stress triaxiality ratio [3-6]. Other studies considered morphological parameters such as the molecular weight and the degree of crystallinity [7-9]. However, most of these studies dealt with uniaxial tensile, compression test, and creep test.

The change in mechanical properties due to different loading histories was widely reported in literature [1, 10-12], however, all of these conditions were not totally fulfilled. Indeed, limited studies were carried out to investigate the volume strain under large deformation at various conditions and tests that generate very complex memory effects, such as cyclic recovery test, uniaxial strain rate jump test and cyclic tensile tests in large deformation at different maximum strain levels.

Despite the availability of many mechanical models developed to characterize the plastic damage deformation of polymers under uniaxial monotonic and cycling tests which induced strain deformation accompanied with volume change [2, 9, 12-13], limited researches were carried out to investigate the effect of loading history on the response of semi-crystalline to complex loadings in large strains. Moreover, these models deal with small or moderate strains and do not predict the variation of volume strain which is observed experimentally.

In this work, the first part is concerned with the experimental investigation and analysis study to obtain the evolution of nonlinear behaviour and volume strain in large deformation of semi crystalline polymers due to the change of loading paths in order to determine the effects of loading history. In the second part, the behavior of the high density polyethylene is compared to that obtained by simulation using a uniaxial constitutive model which can describe the stress unloading, reloading and strain recovery stages. The developed model is formulated based on a non-equilibrium thermodynamic approach of irreversible processes.

EXPERIMENTAL PROCEDURE

The test material is 6 mm thick extruded sheets of high density polyethylene produced by Röchling Group. The HDPE employed in this study is denoted as Polystone® D (PE-HMW/PE 500) by the supplier. Material analysis was carried out using differential scanning calorimetry (DSC), and X-ray showed that the crystallinity ratio is about 66 %. The glass transition temperature and the melting point are -125˚C and 135˚C, respectively. Additional data for the material is listed in Table (1).

Table 1: Characteristics of HDPE used in this study

Density	Molecular weight	Yield stress	Modulus of elasticity	Elongation at Break	Service temperature range
g/cm^3	g/mol	N/mm^2	N/mm^2	%	C^o
0.952	500,000	27	1200	50	-100 to 80

Test specimens were cut from extruded sheets by milling along the extrusion direction which represents the isotropic case where transverses strain ε_{22} and ε_{33} are equal. This was proved for the same extruded sheet by Rida et al [14]. To ensure the localization of the deformation (necking) in the central part where the mechanical variables are determined, a Bone-shaped geometry was designed as shown in Figure 1, where the stress is maximum in the central part and the deformation always initiates in this area.

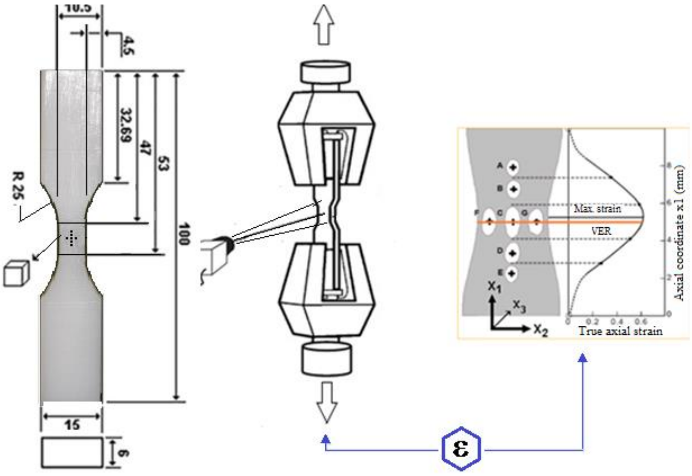

Figure 1: Illustration of tensile specimen set-up and geometry (dimension in mm).

Experimental Set-up

An accurate deformation measurement is needed to measure and quantify the nonlinear behaviour of polymers. Inhomogeneous deformation and necking in this kind of materials usually occur at relatively small strain, therefore the validity of traditional extensometers is useless to evaluate the evaluation of volume strain in large inhomogeneous deformation of polymers. Several experimental techniques were developed to measure the volume strain of polymers during the mechanical tests, with significant improvements in terms of flexibility and precision.

The optical extensometers (e.g. the Videotraction [15] or DIC, Digital Image Correlated, [16]) are now the most adopted experimental methods for large deformation which allow analysing the evaluation of volume change in a quantitative way. The testing systems are designed in such a way that allow the stresses and strains is continuously assessed and controlled while the material undergoes plastic instabilities, damage, strain hardening and failure.

All different types of mechanical tests were performed at controlled room temperature on a servo-hydraulic MTS 810 equipped with a videometric testing system for measuring the true strain without any contact with specimen, called Videotraction. This system gives access to the true mechanical behaviour of polymers for different deformation paths, the volume change of polymer under test can be monitored by determining in real time the true strains in a representative volume element (RVE) situated at the center of the neck. The details of this technique were previously published in [15]. By using CCD camera, and an image analysis software, the mechanical variables were determined by analyzing the displacements of seven dot markers printed on the main face of the specimens. Five vertical marks were aligned in the tensile direction for a precise measurement of the true strain in the tensile direction ϵ_{11}, and the two others being aligned with the central dots along the transverse axis as shown in Figure (1).

To investigate the influence of loading history on the mechanical properties of HDPE, several loading paths mainly in uniaxial tension was applied on this material up to the strain levels of $\varepsilon_{11} = 1.6$. The following experiments were performed:

1- Cyclic tensile tests with various maximum strain levels.
2- Uniaxial loading-unloading-recovery-reloading test.
3- Uniaxial Strain Rate Jump test.

To take into account the variability of the measured responses, the reported experimental results concern three to five series of tensile tests under the same testing conditions. The reproducibility of the results was checked by comparing the different stress–strain curves as well as the volume strain curves, during uniaxial monotonic tensile tests at various strain levels. Good agreement of the results was obtained as shown in Figure (2). A particular attention was drawn on the necking phenomenon, which appeared in the central area of the specimen where the three dot marks were aligned perpendicular to the tensile axis. To avoid buckling of sample during unloading stage, an anti-buckling system was used.

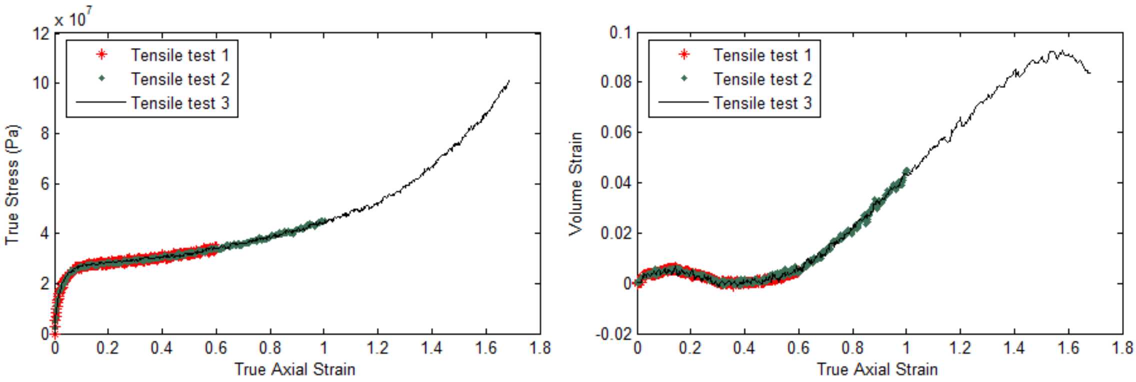

Figure 2: Reproducibility of tests at various strain levels, T=23 C° and strain rate of $10^{-3}\ s^{-1}$ for True stress and volume strain vs. true axial strain curves.

EXPERIMENTAL RESULTS AND DISCUSSION

Monotonic and Uniaxial loading/unloading/reloading tensile test

The evolution of true stress and volume strain obtained from the uniaxial monotonic tensile tests of HDPE specimens are presented in Figure (3). A typical highly elasto-viscoplastic behavior is observed. Up to the yield point, the HDPE exhibits viscoelastic behavior, while beyond this point, a homogeneous plastic deformation took place characterized by a progressive strain hardening associated to the propagation of necking. The evolution of volume strain of HDPE shows a trend with the three regions, at very beginning of deformation and up to the yield point, there is a monotone increase of volume strain observed, which may be attributed to the contributions from elastic expansion and cavitation's [5, 17-18]. A maximum of 0.005 is reached when the strain is around 0.1. Beyond this point and below strain level of 0.5, the volume strain decrease approximately to zero, this may be attributed to the volume compaction of the amorphous due to rearrangement of lamellae orientation accompanied by the changing of voids shape and/or to the closure of small cavities initially presented in the HDPE [19-21]. When the strain is larger than 0.5, the volume strain increases significantly which seems to be connected to the formation and growth of cavities [5-6, 17-18].

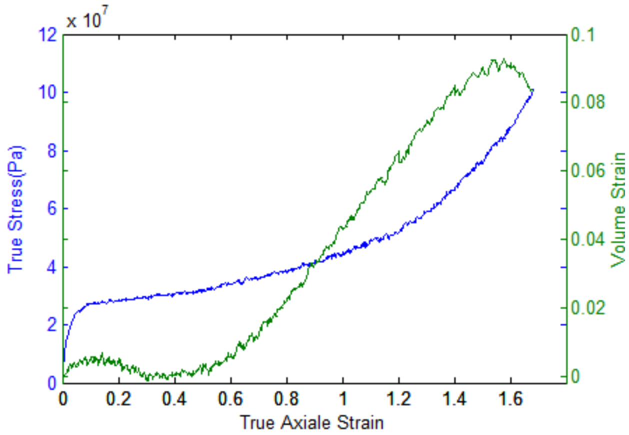

Figure 3: Evolution of true stress and Volume strain vs. true axial strain during Monotonic tensile tests an at strain rate of 0.001s^{-1}.

Figure (4) shows the evaluation of true stress and volume strain curves as a function of true strain for HDPE subjected to uniaxial cyclic tensile loading at several strain levels with a constant strain rate 0.001s^{-1}. In this test, in each cycle with the same strain rate, the HDPE was loaded up to a certain maximum strain, unloaded down to the zero stress, then reloaded up again to maximum strain etc. The test consists of 3 cyclic loadings which involves at least 14 cycles of deformation. Similar observations were reported by [22, 23] for HDPE but for small strains, which is different in contrast to this work as the large strain and volume strain during the cycles is considered. As shown in figure 4, the true stress – true strain curve presents a strong nonlinear and viscoelastic recovery behavior during cyclic loading. The area including in hysteresis loops is large initially, and it decreases with number of cycles, which means that some damage occurs. The increasing of cycle number does not lead to disappear of hysteresis loops curves but they tend to superimposed. It is apparent that maximum true stress decreases with the increase of cycle's number. The decrease is sharp at the beginning and then becomes gradual. The residual plastic strain, corresponding to zero stress, increases substantially in the first three cycles of deformation and then becomes gradual.

For the volume strain, in Figure (4), a considerable decrease in the volume strain during unloading path due to contraction of material. Indeed, it can be clearly seen that the significant linear stage leading to a very small hysteresis loops, contrarily to the stress responses, the hysteresis loops are very small especially at large strain, this effect will disappear and the volume strain tends to stabilize around specific values at greater numbers of cycles. This contrasts to results of continuous tensile loading where no cyclic hardening effect is observed during the tests, and the interruption by unloading reloading cycles does not have any change on the stress and volume strain responses memory.

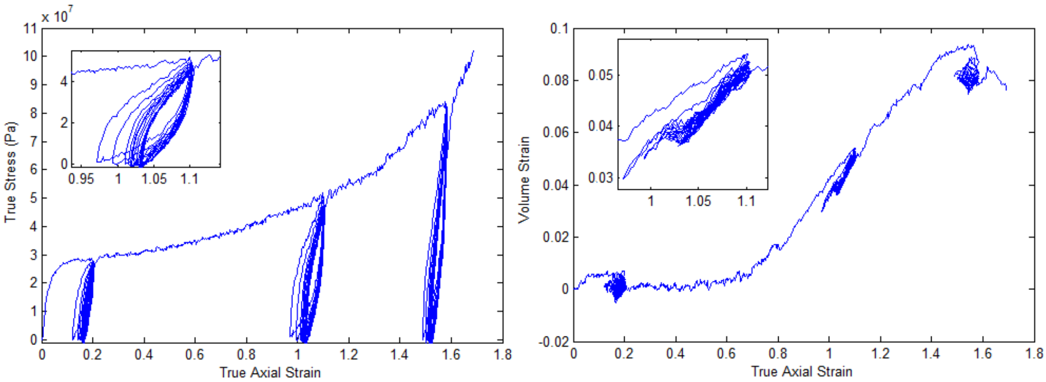

Figure 4: Evolution of true stress and volume strain vs. true axial strain, in cyclic tensile tests with various maximum strains ε_1^{max} at strain rate of $0.001s^{-1}$.

An interesting finding of this test is that, the cyclic damage leading to increase of the average slop of the hysteresis loops with increasing number of cycles, which means that some damage occurs, and can be represented by the effective or apparent Young's modulus. This damaged modulus is determined as the slope of a straight line connecting points of maximum and minimum on the stress-strain curve, which is generally not equal to the initial Young's modulus, and it is an indication of the stiffness change of the material induced by Material damage. Therefore, the evolution of apparent Young's modulus with respect to the number of cycles can be characterized by measuring the slopes of unloading–reloading as the strain increases, as widely reported for highly nonlinear materials during cyclic loading [23-25]. The apparent Young's modulus is strongly influenced by the amount of number of cycles as shown in Figure (5). The values of modulus increased when the number of cycles increased until it tends to stabilize around specific value at greater numbers of cycles.

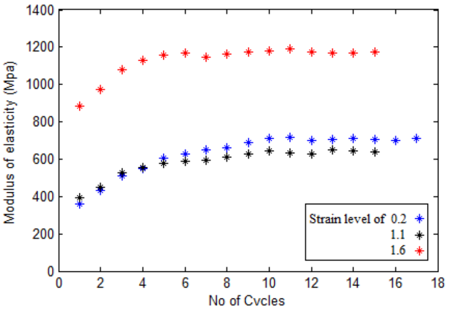

Figure 5: Variation of the apparent Young's modulus vs number of cycles during cyclic tensile tests strain rate of $0.001s^{-1}$.

Uniaxial Loading-Unloading-Recovery Tests

The evolution of true stress and true volume strain for seven tensile test specimens during loading/unloading and recovery tests are presented in Figure 6. The curves consist of three portions in accordance with three loading paths (i.e. loading, unloading and holding), each test series were stretched until a particular strain level (path 0 to 1) followed by unloading to the zero stress (path 1 to 2) at the same strain rate of 0.001 s^{-1}, then the sample was kept at the zero stress to recover (path 2 to 3) for a sufficiently time until there was no change of the measured axial strain at Point 3. In fact, there is no remarkable change in axial strain and volume in the period between 3 hours and 24 hours during recovery stage which was verified experimentally, and it is consistent with previous observations obtained by [5].

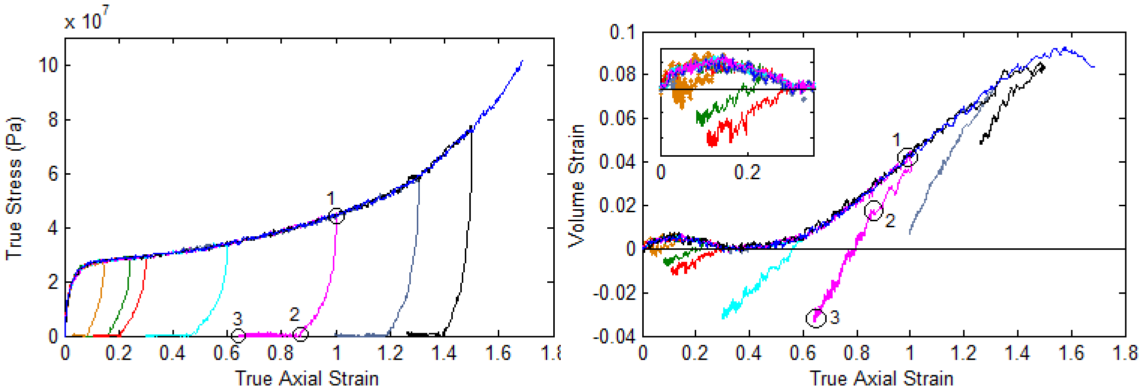

Figure 6: Evolution of true stress and volume strain vs. true axial strain during uniaxial loading/unloading/recovery test at different levels of axial strain and strain rate of 0.001s^{-1}.

The volume strain decreases during unloading and recovery stages, and this decrease varies with the axial strain and becomes more important in recovery stage. Even at the end of recovery, a residual volume strain is not yet equal to zero. According to the experimental results, the Damage evolution presented by volumetric strain in Figure 7 can be divided into three components, $\varepsilon_v = (\varepsilon_v)_{elastic} + (\varepsilon_v)_{cavitation} + (\varepsilon_v)_{recovery}$, Where $(\varepsilon_v)_{elastic}$ represents the volume strain during unloading path (1 to 2) induced by elasticity, $(\varepsilon_v)_{cavitation}$ is the volume strain measured at zero stress attributed to the contribution of cavitation or crazing, and $(\varepsilon_v)_{recovery}$ is the volume strain during the recovery path (2 to 3).

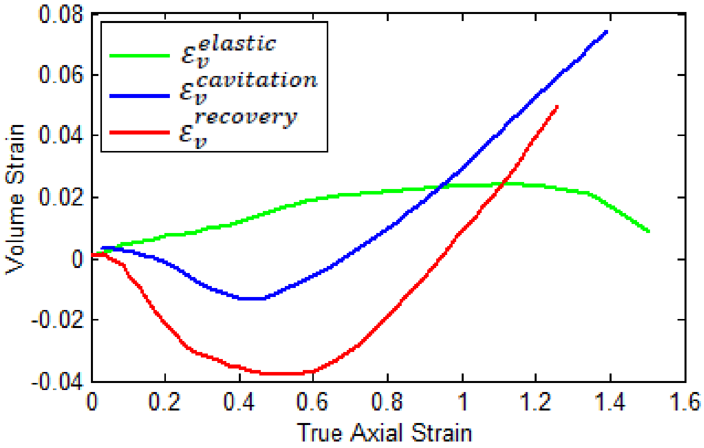

Figure 7: Components of volume strain during uniaxial loading/unloading/recovery test.

It is evident that until yield point, no volume strain due to the damage is observed, and the dilatation effect associated with elastic deformation is the dominant mechanism. Whatever the deformation level is, the contribution of strain volume induced by elasticity is always positive. The onset of $(\varepsilon_v)_{cavitation}$ and $(\varepsilon_v)_{recovery}$ contributions occur beyond the yield point, whereas the cavitation of the first voids begins approximately at the yield [26]. As the applied axial strain increases, those contributions to the total strain, respectively decreases and increases. This occurs during the unloading stage due to the volume contraction of the amorphous when the rearrangement of lamellae orientation is accompanied by the changing of voids shape and/or to the closure of small cavities as initially presented for the HDPE [27- 29]. While during the recovery stage, it is related to the phenomena of spring back of the amorphous chains which are mobile at room temperature [5]. The variation of volume strain is maximum for moderate axial strains where the most important compaction in residual volume strain occurs between the yield point and axial strain approximately equal to 1 (associated to the propagation of necking), while residual volume strain remains positive for higher applied axial strains.

Uniaxial Loading-Unloading-Recovery-Reloading Test

It is of the current research interest to investigate the effects of recovery time on the evaluation of volume strain of the HDPE considered. This was performed by subject only one tensile specimen to a cycle of deformation at different strain levels, which consists of applying a loading/unloading to zero stress/recovery for 3 hrs. and then reloading. The evolutions of stress and volume strain versus strain in these tests are presented in Figure (8). An instantaneous increase in stress and volume strain is observed immediately after the reloading is increased. Both the stress and volume strain attain the level they have before beginning of the unloading stage.

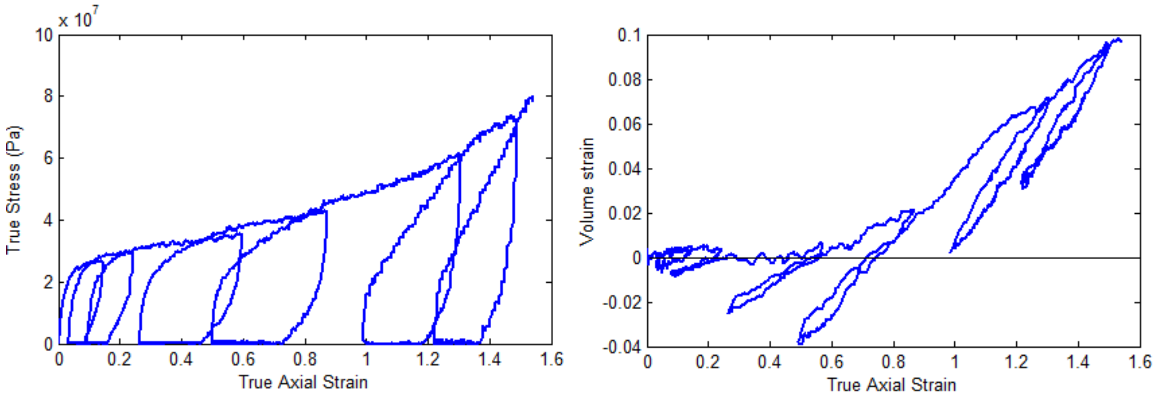

Figure 8: Evolution of axial stress and volume strain vs. axial strain during uniaxial loading/unloading/recovery/reloading test at strain rate of 0.001s^{-1}.

At the beginning of reloading, which is the elastic region, both axial and volume strain increase with the same kinetic as that during the previous recovery, then the evolutions of volume strain caused by micro-voids undergoes reopening in the same way as they closed during previous unloading stage. Finally, with the continuing of loading and when plastic flow region is reached, damage increases and strongly accelerates in comparison with the previous cycle. In contrast to the monotone tensile results, the envelope formed by these cycles coincides very well with the true stress and true volume versus strain curves of the single tensile test. The memory of previous stress and volume strain conserved, this indicates that the unloading and recovery stages have no effect on the stress or evolution of volume strain (there is no history dependency).

Effect of Strain Rate and Strain Rate Jump Test

Further analysis to study the effect of strain rate history on the elasto-viscoplastic behavior, particularly on volume strain response of HDPE was performed. Therefore, tests have been carried out at large deformation under series of uniaxial tensile tests at several constant strain rates and strain rate jump tests as presented in Figure (9).

For monotonic tensile test with three different strain rates, the influence of different strain rate on stress and volume strain is shown in Figure (9). It is shown that the true stress increases remarkably at all strains levels as the strain rate increases, as expected, and this is reported in many studies [5,9,30]. Below the yield point, the yield stress and the initial young's modulus shows strain rate dependent. The HDPE shows a strong influence of the strain rate on the volume strain evolution. It is clear from the results that; no change can be observed in the dilatation before the yield point; hence there is no strain rate dependent. Once the plastic stage begins, volume strain evolution shows compaction and dilatation successively for all strain rates, and the volume compaction phenomenon decreases as the strain rate increases, and for the higher strain rates, the onset of the volume dilatation took place much earlier.

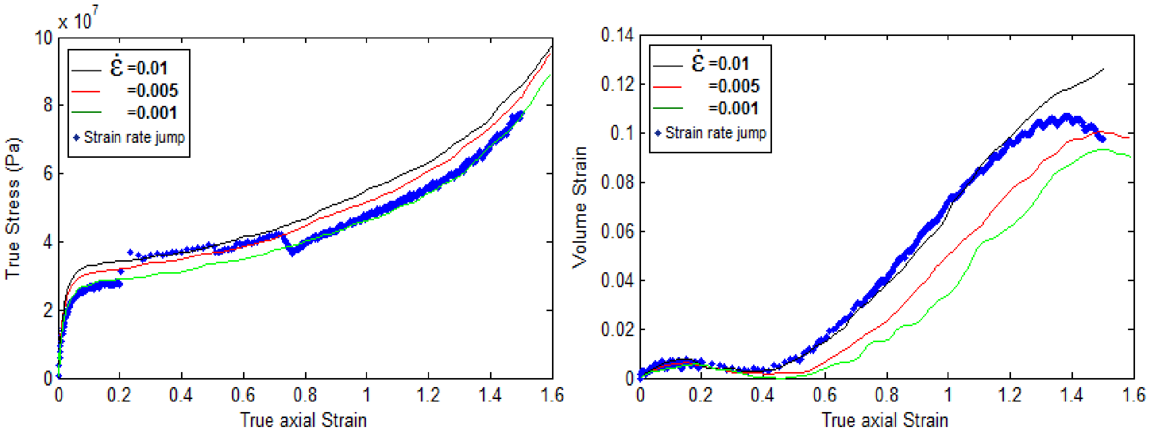

Figure 9: Experimental results for uniaxial tensile tests at several constant strain rates and strain rate jump test.

Figure (9) also shows the results obtained from a sudden change of strain rate, and strain rate jump, where the strain rate varies during a single test. The initial strain rate was equal to 0.001 s^{-1}, and is increased to 0.01, then decreased to 0.005 s^{-1} for selected time intervals, then decreased once again to its initial strain value of 0.001 s^{-1}. An instantaneous stress increase or decrease immediately was observed after increasing and decreasing the jumps respectively. The stress attaints the level it would have which is the same if the new strain rate had been used from the beginning of the test. Hence, the interruption by the strain rate jump does not change the memory of the previous strain rate. This test indicates that the stress response of HDPE does not have strain rate history dependency. Contrarily for the evaluation of volume strain, the memory effect during the transient region of strain rate change is very significant as the volume strain increases with the increase of the strain rate. However, the HDPE keeps this change in volume although the strain rate returns to its initial value. One can attribute this phenomenon to the micro-cavities, which are already created during the deformation in the material, which does not change its size even after decreasing the strain rate. Therefore, the volume strain evaluation of HDPE has a highly strain rate history dependency.

THERMODYNAMIC MODELLING

In this part, a constitutive model is developed in order to describe the mechanical behavior of HDPE subjected to several complex loading paths even at large deformation taking into account the strain recovery, strain rate and volume variation due to damage effect. The modelling proposed is based on previous models of Cunat et al [31-32] and Kais et al. [33, 14]. This model is based on the non-equilibrium thermodynamic approach named, DNLR (Distribution of Non Linear Relaxation), which is presented in details in [31,32]. It is based on the study of the internal rearrangements such as relaxation process from a thermodynamic point of view; that is the thermodynamic of irreversible processes. The model allows to describe the mechanical behavior even outside of equilibrium, and the evolution of a RVE of materials submitted to the controlled perturbation.

General Formulation of Distribution of Non Linear Relaxation Approach

Typically, one can assume the existence of a thermodynamic potential of non-equilibrium, $\psi(\underline{\gamma}, \bar{z})$, which completely describes the state of the material. This potential depends on the control state variables $\underline{\gamma}$ necessary to characterize the non-dissipation evolution of RVE, the internal microstructural variables $\bar{z}$, and dissipative variables which represent different internal reorganization associated to their dual forces $\underline{\beta}$ and $\bar{A}$, respectively. Subjected to an external perturbation, $\underline{\gamma}$, the material response $\underline{\beta}$ is due to multiple internal reorganizations and it is described by nonlinear incremental law. In this approach, the general constitutive equation of DNLR is decomposed into an instantaneous or unrelaxed component (referred as with index u) and a dissipative or relaxed component (referred as with index r) which is characterized by two original features:

1) distribution of the dissipation processes including nonlinear effects is obtained by an extension of the fluctuations theory,
2) modelling of the relaxation time response based on activation state theory.

In the case of mechanical problem, and by replacing β and γ by the stress σ and strain ε, respectively, the general tridimensional relation of DNLR approach can be written as:

$$\dot{\sigma} = \sum_{j=1}^{N} \dot{\sigma}^{j} = \sum_{j=1}^{N} \left(P_0^{j} \, E^{u} \, \dot{\varepsilon} - \frac{\sigma^{j} - P_0^{j} \sigma^{j,r}}{\tau_j^{r}} \right) \tag{1}$$

Where $\dot{\sigma}$ is the global response of the material (sum of each modal stress $\dot{\sigma}^{j}$), which is decomposed in two parts, elastic or instantaneous response represented by $\left(P_0^{j} \, E^{u} \, \dot{\varepsilon}\right)$ for a mode j, and dissipative part governing the evolution of relaxed state for each mode j by $\left(\sigma^{j} - P_0^{j} \sigma^{j,r} \big/ {}_{j}^{r}\right)$. N is the number of dissipative modes. The weight P_0^{j} of each mode is obtained by an extension of the fluctuation theory which leads to [33],

$$P_0^{j} = \frac{\sqrt{\tau_j^{r}}}{\sum_{j=1}^{N} \sqrt{\tau_j^{r}}} \tag{2}$$

Where τ_j^{r} the relaxation time of each mode j, to model the relaxation times one can use the following classical relation [31,32]:

$$\tau_j^r = \frac{h}{k_B T}\exp\left(\frac{\Delta F^+}{RT}\right)\left(\frac{-V\left|\sigma \ - \sigma^r\right|}{RT}\right) = \tau_{\max}^r \, a(t) \tag{3}$$

$a(t) = \exp\left(-V\left|\sigma \ - \sigma^r\right| / RT\right)$ represents the nonlinearity shift factor associated with the activation volume average *V*, $\Delta F_j^{+,r}$ represents the activation Helmholtz free energy of the spontaneous fluctuation around the relaxed state for the dissipation mode *j*. *h*, *k_B* and *R* are constants of Plank, Boltzmann and perfect gases, respectively. *T* represents Kelvin temperature. The definition of the role of the relaxed state σ^r and the relaxation times τ^j is very important step to describe the evaluation of dissipative part.

Damaged Model for Semi-Crystalline Polymers

The experimental investigation reveals that the elasto-viscoplastic behaviour of semi crystalline polymers is related to their spherulitic microstructures, constituted by amorphous and crystalline phases. It well known that the mechanical behavior depends strongly on the microstructural changes in the two phases during plastic deformation [5,9,11]. Thus, in our case of HDPE, it must take into account the microstructural changes mechanism and the existence of two phases which is the key in determining the overall macroscopic mechanical behaviour of HDPE as reported by [14]. Therefore, to entirely describe the state of material under unidirectional mechanical tests, the DNLR approach can be reformulated by chosen a new thermodynamic potential as $\phi = \phi\left(\varepsilon, T; \bar{z}; \bar{\rho}; \bar{e}\right)$. In this potential three distinct internal reorganization families are considered. The first one, $\bar{z}$, is related to the relaxation mechanisms that depend on the imposed strain rate (viscous process)) mainly due to the amorphous phase. The second, $\bar{\rho}$, is related to the non-viscous mechanisms that are independent of this strain rate (plastic process) which one can physically connect to the fragmentation of crystalline lamellae. Last family ($\bar{e}$) is corresponding to the phenomena of damage by cavitation.

By applying this new thermodynamic potential for uniaxial mechanical test with imposed strain $(\dot{\varepsilon}_1, \varepsilon_1)$, the components $\sigma_1, \varepsilon_2 \ and \ \varepsilon_3$ can be measured. Knowing that the lateral principal stresses $\sigma_2 = \sigma_3 = 0$, can be treated as controlled variables. The different developments of the model which is well described in [14], lead to the following constitutive equations of the DNLR approach for uniaxial solicitation:

$$\dot{\sigma}_1 = \sum_{j=1}^{N} \dot{\sigma}_1^j = E_1^u \, \dot{\varepsilon}_1 - \sum_{j=1}^{N} \left(\frac{(\sigma_1^j - P_j^0 \sigma_1^{j,r})}{\tau_j^r}\right) \tag{4}$$

$$\dot{\varepsilon}_2 = \sum_{j=1}^{N} \dot{\varepsilon}_2^j = -\nu_{12}^{r,eff} \, \dot{\varepsilon}_1 - \sum_{j=1}^{N} \left(\frac{\delta_{12}}{E_1^{r,eff}} \frac{(\sigma_1^{j,r} - P_j^r \sigma_1^{j,eq})}{\tau_j^{eq}}\right) \tag{5}$$

$$\dot{\varepsilon}_3 = \sum_{j=1}^{N} \dot{\varepsilon}_3^j = -\nu_{13}^{r,eff} \, \dot{\varepsilon}_1 - \sum_{j=1}^{N} \frac{\delta_{13}}{E_1^{r,eff}} \frac{(\sigma_1^{j,r} - P_j^r \sigma_1^{j,eq})}{\tau_j^{eq}} \tag{6}$$

$$tr\,\underline{\underline{\dot{\varepsilon}}} = \dot{\varepsilon}_1 + \dot{\varepsilon}_2 + \dot{\varepsilon}_3 \tag{7}$$

With $$\dot{\sigma}_1^r = \sum_{j=1}^{N} \dot{\sigma}_1^{j,r} = E_1^{r,eff} \, \dot{\varepsilon}_1 - \sum_{j=1}^{N} \left(\frac{(\sigma_1^{j,r} - P_j^r \sigma_1^{j,eq})}{\tau_j^{eq}}\right) \tag{8}$$

Where E_1^u are the instantaneous modulus of elasticity, $E_1^{r,eff}$ & $\nu_{12}^{r,eff}$ and $\nu_{13}^{r,eff}$, are the damaged modulus of elasticity, and damaged Poisson's ratios at relaxed state, respectively. σ_1^{eq} is equilibrium stress corresponding to their relaxation time τ_j^{eq} of the mode j, controlling the phenomenon of relaxation from the relaxation state to the equilibrium state associated with their weight obtained by $p_j^r = p_j^0 + \left(p_j^u - p_j^0\right)/2$, with $p_j^u = 1/N$ [33]. δ_{12} & δ_{13} are the model parameters to be adjusted?

The equilibrium stress evolution, σ_1^{eq}, is governed by 8-chain model proposed by Arruda and Boyce [34]. This model is capable to reproducing the hyperelastic hardening at large strain of rubbers, due to reorientation and changes in molecular chains configuration. This model which physically based on the non-Gaussian statistical mechanics models provides a constitutive law that requires only two material properties, N0 the number of chains per unit volume, and n the number of rigid segments per macromolecular chain. In the case of uniaxial loading, the expression of σ_1^{eq} is given by:

$$\sigma_1^{eq} = \frac{N_0 k_B T}{3\lambda_c} n^{0.5}\left(\lambda_1^2 - \lambda_2^2\right)\ell^{-1}\left(\frac{\lambda_c}{n^{0.5}}\right) \tag{9}$$

With $\lambda_1 = \exp(\varepsilon_1)$, $\lambda_2 = \exp(-\varepsilon_1/2) = 1/\sqrt{\lambda_1}$, $\lambda_c = \sqrt{\lambda_1^2 + 2\lambda_1^2/3}$, and $\ell^{-1}\left(\lambda_c/n^{0.5}\right)$ is the inverse of the Langevin function. The term $N_0 k_B T$ represents the initial shear modulus.

Extension for Strain Rate Effect Consideration

The effect of strain rate with respect to the independency of the relaxed state of the strain rate that agrees with the experimental results of ROGUET et al [35,36] is taking into account in this work, where the effect is introduced in the nonlinearity shift factor, $a\ (t, \dot{\varepsilon}\ )$ which will take place in both τ_j^r and τ_j^{eq}. The relaxation spectrums which control the phenomenon of relaxation from the instantaneous state to the relaxation state and from the relaxation state to the equilibrium state are respectively written as:

$$\tau_j^r = \tau_{\max}^r \exp\left(\frac{-V\left|\sigma \ - \sigma^r\right|}{RT}\right)\left(\frac{\dot{\varepsilon}_0}{\left|\dot{\varepsilon}\ \right|}\right)^{1/m} \tag{10}$$

$$\tau_j^{eq} = \tau_{\max}^{eq} \exp\left(\frac{-V^{eq}\left|\sigma^r - \sigma^{eq}\right|}{RT}\right)\left(\frac{\dot{\varepsilon}_0}{\left|\dot{\varepsilon}\ \right|}\right) \tag{11}$$

The term $\left(\dot{\varepsilon}_0/\left|\dot{\varepsilon}\ \right|\right)^{1/m}$ represents the effect of strain rate, m is the strain rate sensitivity factor. For (m=1), the material behaviour is independent of strain rate as in the relaxed state. $\dot{\varepsilon}_0$ is the critical strain rate below which the tensile behaviour is no more dependent on the strain rate [33,34]. $V = V_0 \exp(k_1 \varepsilon^{\ k_2})$, where V_0 is the activation volume which increasees with deformation (damage effect), k1 and k_2 are the parameters. $\tau_{\max}^{eq} = h/k_B T \exp\left(\Delta F^{+,eq}/RT\right)$ and V^{eq}, the activation volume which is related to the fragmentation /orientation mechanisms of crystallites lamellae.

Damage Effects

The experimental results showed that the damage may be represented by an elastic properties change which is strongly strain dependent [2,14]. This can be attributed to the occurrence of two physical phenomena. The first is the microstructural damage with a significant decrease in the elastic modulus associated with lamellar fragmentation and microcavities. The second is the densification due to the strain hardening with significantly increased in the elastic modulus resulting from molecular reorientation [14]. To describe the nonlinear behavior of HDPE during unloading, improvements of modelling capabilities are now proposed. The evolution of damaged modulus of elasticity at relaxed state, $E^{r,eff}$, and the damaged Poisson's ratios at relaxed state, $\nu_1^{r,eff}$, can be modelled by considering two physical phenomena, therefore the following empirical expression is proposed:

$$
\begin{aligned}
E_1^{r,eff} &= E_1^r\,[1 - D_{11}], \\
\nu_1^{r,eff} &= \nu_{12}^r\,[1 - D_{12}\,]
\end{aligned}
\qquad (12)
$$

Where D_{11} and D_{12} are the damage variables resulting from the two contributions $D = D_{cavitation} + D_{orientation}$, the first contribution, $D_{\text{cavitation}}$, leads to the decrease in the elastic modulus while the second contribution, $D_{orientation}$, leads to the increase in the elastic modulus.

In most constitutive models, the evolution of $D_{\text{cavitation}}$ is expressed by $\alpha_1(1-\exp(-\beta_1\varepsilon_1))$ where a classical definition of the damage variable is used to capture the decrease of the elastic modulus of polymers especially in small strain. This differs from the current research where large strains are considered, thus there is an increase in these modulus due to the effect of stretching and reorientation of the chains. Therefore, to describe an evolution equation for $D_{orientation}$, the proposed model attempts to utilize the number of segments per chain and takes into account the inverse of the Langevin function similar to that employed in the Arruda and Boyce model [34], which can be expressed as:

$$
D_{orientaion} = \mathrm{X}\ \ell^{-1}\left(\frac{\lambda_c}{n^{0.5}}\right) \qquad (13)
$$

With $\mathrm{X} = (1/n^{0.5})^{0.5}(3n\ \ -1/n\ \ -1)$, n the number of rigid segments per macromolecular chain and $\lambda_c = \sqrt{\lambda_1^2 + 2\lambda_1^2/3}$.

The above equations can be written in the following form:

$$
E_1^{r,eff} = E_1^r \left[1 - [\alpha_1(1-\exp(-\beta_1\varepsilon_1)) - \mathrm{X}\ \ell^{-1}(\frac{\lambda_c}{n^{0.5}})] \right] \qquad (14)
$$

$$
\nu_1^{r,eff} = \nu_{12}^r\,[1 - [\alpha_{12}(1-\exp(-\beta_{12}\varepsilon_1)) + \varepsilon_1^2\,]] \qquad (15)
$$

with α_1 represents the level of maximum damage, β_1, α_{12} and β_{12} (characterizing the damage evaluation) are the parameters to be adjusted.

Finally, with $\dot{\varepsilon}_3 = \dot{\varepsilon}_2$ for transversally isotropic strain case, which is experimentally proved for this HDPE in the extrusion direction, one can write the evolution of the volume strain as:

$$
\dot{\varepsilon}_v = \dot{\varepsilon}_1 + 2\dot{\varepsilon}_2 \qquad (16)
$$

RESULTS OF SIMULATION

The proposed model is validated with the experimental data to demonstrate the capability of the model to produce a strong nonlinear behavior of HDPE during the complex loading conditions applied experimentally on HDPE. The model has been coded by an explicit integration scheme in Mat lab used to numerically integrate our model of nonlinear differential equation. Values for the required material parameters for this material are given as following:

E^u = 1150 MPa, V_0 = -1191.3 $cm^3/Mol\,at$, k_1 =0.56, k_2 = 1.99, $\tau^r_{\max}$ = 20100 sec, $E^{r,eff}$ = 265 MPa, α_1= 0.89, β_1 = 18, $\tau^{eq}_{\max}$ = 19×10^7 sec, V^{eq} = -520 $cm^3/Mol\,at$, $\dot{\varepsilon}_0$ = 10e^{-7} sec, m= 0.18, Nk_BT = 0.53 MPa, n= 90, v^r_{12} =0.525, α_{12} =0.2235, β_{12} =-1.580, δ_{12} =0.059.

Based on the previous experimental data, these parameters were identified using the optimization SiDolo software. It should be mentioned that these parameters were used in all simulations presented in this section. The cyclic recovery reloading test of HDPE is simulated and predicted by the proposed model as shown in Figures (10). It can be seen that the capacity of the model to predict successfully the evolutions of stress even after recovery stage at different strain levels, and the recovery residual strain after the unloading stage. For the volume strain, a quite nice agreement is observed between the predicted behaviour and experimental results even at large deformation.

The nonlinear response of these materials under unloading and reloading is shown in Figure (11). It is shown that the model captures the experimental data for the excessive cyclic responses. It is also observed that the hysteresis loops, the amplitude, the mean stress and the phenomena of tendency to loop superimposed are well simulated. Figure (12) shows the simulated stress response of strain rate Jump test with the same set of material parameters which used above. The model can take into account the influence of strain rate and correctly predict the behavior and strain rate history on the elasto-viscoplastic behavior for HDPE.

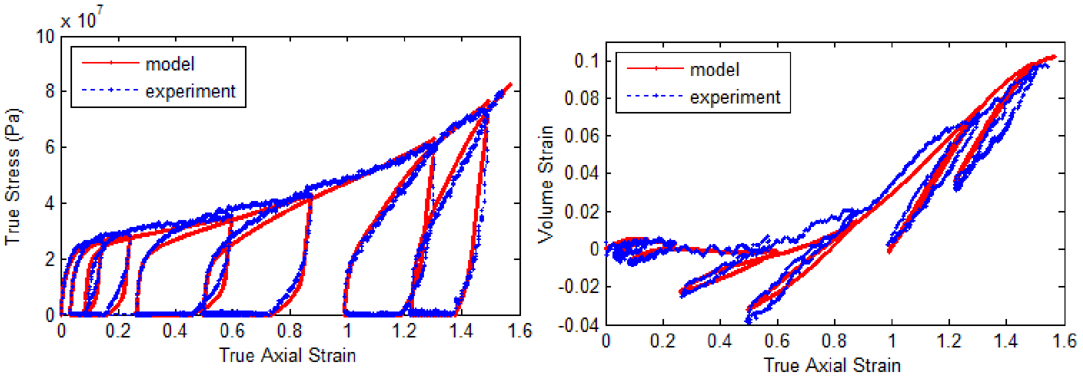

Figure 10: Results of simulation for true stress- strain and for volume strain curve during cycling uniaxial loading/unloading/recovery/reloading test at strain rate of 0.001s^{-1}.

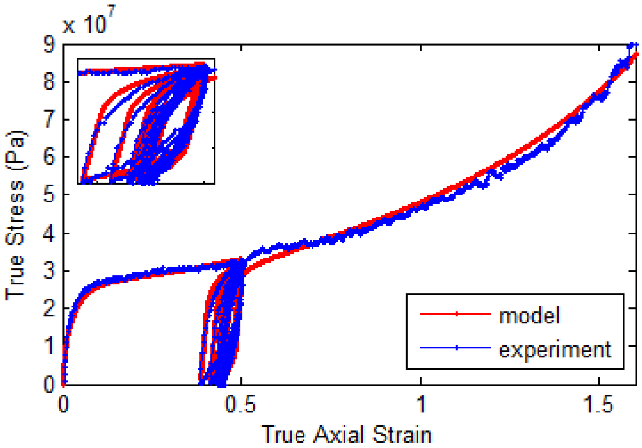

Figure 11: Results of simulation for true stress- strain and for volume strain curve during uniaxial cyclic tensile tests at strain rate 0.001 s^{-1}.

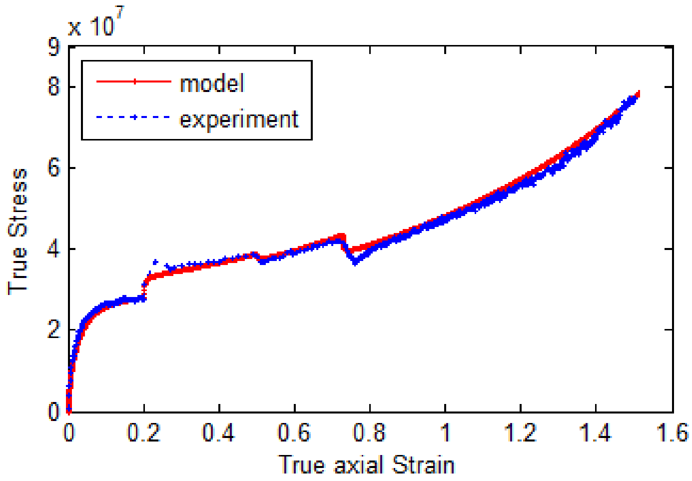

Figure 12: Results of simulation for true stress- strain and for volume strain curve during strain rate jump test.

CONCLUSIONS

In this paper, the nonlinear behaviour of high density polyethylene (HDPE) and effects of loading history under large strains are investigated. Several experimental tests with different loading conditions were carried out on a hydraulic testing machine equipped with the optical Videotraction extensometer. This technique allows simultaneous measurement in real time of the stresses and strains under a controlled rate of axial strain. Volume changes were measured during these complex tests which revealed that the damage process is significant and must be taken into account.

The experimental results showed that the mechanical response of the HDPE is highly nonlinear and there is no significant effect by changing the orientation of loading during the cycling recovery and cycling deformation tests, no history dependency for the stress and volume strain was found. Contrary for strain rate effect, the mechanical behavior of HDPE is significantly affected by the strain rate. No strain rate history dependency for the stress response was found during strain rate jump test, but it shows a high history dependency for volume changes.

A constitutive model for the large deformation of semi-crystalline polymers has been presented. This thermo-mechanical model is based on the thermodynamics of irreversible processes, which allows describing the change in nonlinear deformation behavior during complex loading conditions applied on HDPE. With this model, the effect of damage, strain rate and the loading history on the mechanical response during different loading conditions tests of semi-crystalline polymers was examined. The results of this model simulation for the mechanical response of HDPE were compared to the experimental observations and fair agreement was found.

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