ANALYSIS OF ANNEALING EFFECT AND MACROSCOPIC TRIAXIALITY ON HIGH DENSITY POLYETHYLENE

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This work is devoted to the experimental study of annealing effects on microstructure and mechanical properties of the high-density polyethylene (HDPE). Uniaxial tension tests are conducted at 25 ∘C, in order to characterize the mechanical behavior of HDPE. The influence of the annealing treatment on the material microstructure is characterized using differential scanning calorimetry. It is found that the annealing causes the increase of all properties measured, including crystallinity, melting temperature, Young Modulus and yield stress. Moreover, the creep and relaxation experiments are performed at different stress and strain levels, respectively: in elastic region, prior to yield and viscoplastic region.

Keywords: Annealing, high-density polyethylene, large strain, behavior, damage.

1. Introduction

This paper is concerned with experimental investigation of the viscoelastoplastic responses of semicrystalline polymers after annealing. Correlations between crystalline morphology and mechanical properties in polymers have attracted substantial attention in the past decade [1–4]. Previous studies of structure–property relations focused mainly on structure, whereas mechanical properties have received secondary importance. The present work is devoted to the study of the mechanical behavior of virgin and annealed high-density polyethylene (HDPE). We will focus particularly on the evolution of the Young's modulus, the yield stress and the strain at failure. The challenge is to identify the relation between hold time, crystallinity degree (modified during the annealing process), and mechanical properties.

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1.1. Background on annealing

Previous studies of structure–property relations mainly focused on structure, whereas mechanical properties remained of secondary importance. In recent work, many authors [5-8] note that annealing of polymeric materials after fabrication causes changes in structure and properties of the materials. This process has been employed as a means to improve the final properties of polymers *via* reduction or elimination of defects and residual stress and strain [9]. In addition, the morphological modification of crystal segments via lamellae thickening during heating also occurs in semi-crystalline polymers.

The degree of crystallinity and the size and distribution of the crystallites in a semi-crystalline polymer have a large effect on the mechanical properties of these materials. If the polymer has amorphous structure, inelastic behavior depends on the molecular chain flexibility, entanglement, and on differences in the structure of the molecular chains.

Annealing is known to induce microstructure evolutions also. They were observed by several authors in some crystalline thermoplastics like: ethylene/octene copolymers, Polyether ether cetone (PEEK), Isotactic polypropylene (iPP), amorphous polyethylene terephthalate (PET) or polyphenylene sulfide (PPS) [10–15]. They brought some evidence of a critical temperature (Tc) close to the main melting temperature. Annealing above Tc0 induces a thickening of lamellae. This process requires a great mobility of chains within lamellae. On the contrary, the thickness of primary lamellae remains unchanged during annealing below Tc0: a secondary crystallization is observed, corresponding to the formation of ordered volumes in the amorphous phase. A small endothermic peak is then observed at a higher temperature than the annealing temperature on differential scanning calorimetry (DSC) thermograms. This peak is specific of the melting of these ordered regions located within the amorphous phase. This interpretation was developed by Neidhöfer et al. [16] for alpha- polyvinylidenefluoride (PVDF). In this polymer, the secondary crystallization clearly appears for temperatures as low as room temperature, and is very rapid for annealing at 140 °C. A simultaneous study carried out by NMR shows a decrease of the mobility in the amorphous phase during annealing.

Authors concluded to the existence of conformational constraints induced in the residual amorphous by the formation of secondary crystals. Some correlations to Dynamic mechanical analysis (DMA) experiments were given by El Mohajir and Heymans [17] in the case of a standard annealing at 150 °C on injected specimens of another polyvinylidenefluoride (PVDF) grade.

The results reported on the annealing in polymers are difficult to be compared, since they are generally obtained under different conditions regarding process

parameters. However, this short overview allows giving a general idea of physical processes occurring during annealing of polymers.

1.2 Aim of this work

In this work, our goal is to study the annealing effect, and particularly the hold time, on the mechanical behaviour of the HDPE. The challenge is to identify the relation between crystallinity degrees and mechanical properties. The relative influence of microstructure on mechanical behavior was studied in different macroscopic triaxiality frameworks. Moreover, the creep and relaxation experiments were performed at different stress and strain levels respectively: in elastic region, prior to yield and viscoplastic region.

2. Experimental work

2.1 Initial characteristics of material

The material used in this study consists in granules of PE100, imported by the CHIALI enterprise located at SIDI BELABES (Algeria). PE100 was, then, industrially extruded in order to manufacture tubes of different diameters. This semi-crystalline thermoplastic is constituted of amorphous and crystalline phases presenting themselves as spherulitic aggregation. The molar mass of the HDPE is about 300000 g/mol. Its fusion and glass transition temperatures are 135 °C and -125 °C, respectively.

2.2 Annealing methods

Samples geometries (Diabolo « R=10 » and dumbbell) are put inside the steam room under the following conditions:

- Heating speed of 5°C/min,
- Annealing at 90 °C during different times: 48h, 96h, 144h and 192h.
- Cooling in the steam room.

2.3 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) characterizes polymer phase transformations, particularly the melting of the crystalline phase. Enthalpy variations versus time and temperature were obtained from DSC during controlled heating for five (05) simples before and after annealing.
A PerkinElmer DSC Pyris (Waltham, MA) was used, with a temperature ramp of 10°C/min from 70°C to 200°C. A mass of 1.300 mg is chosen, and precautions are

taken to ensure stable sample specific surface, in order to keep constant thermal transfer coefficient.

The melting temperature of the sample, its crystal weight fraction (χ), were obtained from DSC curves:

$$\chi = \frac{\Delta H}{\Delta H_{100\%}}$$

where ΔH is the sample melting enthalpy (corresponding to the melting peak area), $\Delta H_{100\%}$ the full crystalline sample melting enthalpy (290 J/g by Wunderlich)

2.4 Mechanical study

The stress- strain behaviors of HDPE (before and after annealing) are characterized under uniaxial tensile tests on an electromechanical testing machine. The local strain is measured using a video-controlled system (VideoTraction) consisting in a camera controlled by computer. One of the main advantages of the VideoTraction method is its ability to keep the local true Strain-rate constant [18]. Samples with different shapes (depicted in Fig. 1) were tested to investigate consequences of microstructure changes in different macroscopic triaxiality frameworks. Dumbbell specimens (Fig. 1) were machined in the same extruded sheets as described above with half-scale ISO R527 specifications. Logarithmic axial and transverse strain measurements were analyzed, this technique is based on the follow-up of four (04) markers printed on the front surface of the sample (Fig.2). Two among them are aligned along the tensile direction, the two others according to the transverse direction.

Diabolo specimens with four different curvature radii have been tested to increase the maximum local hydrostatic stress. Geometries are described in Fig. 1. The experimental testing conditions are achieved at ambient temperature and true Strain rate of 10^{-3} s^{-1}. The data acquisition system automatically records the true Stress versus the true Strain.

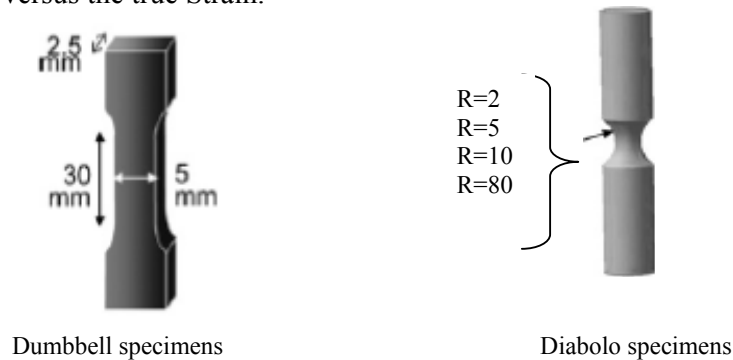
Dumbbell specimens   Diabolo specimens
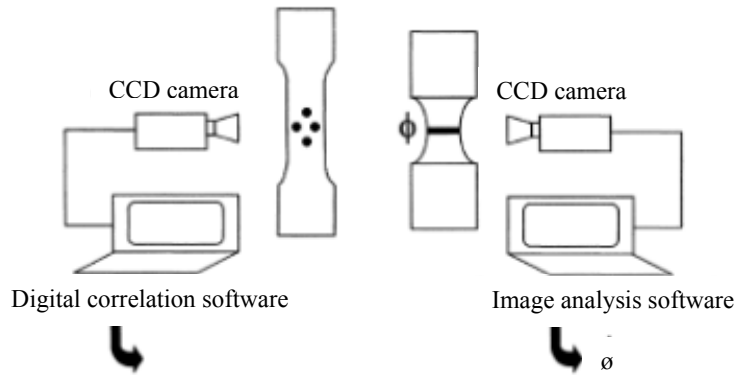
Fig.1 Samples geometries tested in tension

Fig. 2. Extensometer devices used for dumbbell (left) and diabolo (right) specimens.

3. Experimental results

3.1 Virgin HDPE characterization
- **Tensile test**

Fig. 2a shows variation of the stress versus the strain, 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. Plastic compaction (contracting volume strain for intermediate stretching ratio) is in competition with dilatation. This phenomenon appears when the mobility of the amorphous chains and the time to accommodate macroscopic deformation are favored. Using Small Angle X-ray Scattering (SAXS) HDPE specimens, Pawlak suggests that the decrease of the volume strain is a result of rearrangement and orientation of lamellae, accompanied by changing of voids' shape [19]. This explanation, initially proposed by Kahar and al. [20], has been also suggested by G'sell and coauthors [21-23]. When the strain is larger than 0.58, the increase of volume strain is observed (Fig. 2.b). This increase is due to the formation of new cavities, which was also seen in SAXS studies by Pawlak [19]. The final hardening stage is due to microstructural rearrangements and orientation mechanisms, which 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 (Fig. 2.a). 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. 2.c represents the the variation of Poisson's ratio with uniaxial

strain. The curve presents the same shape as those experimentally found by Arieby and Nadège Brusselle-Dupend [27, 24]. In fact, Poisson's ratio is not a constant for polymers. It may be positive, negative, under some loading conditions [25, 26]. For the material considered in this study, the Poisson's ratio values vary from 0,4 to 0,49 in concordance with the theoretical.
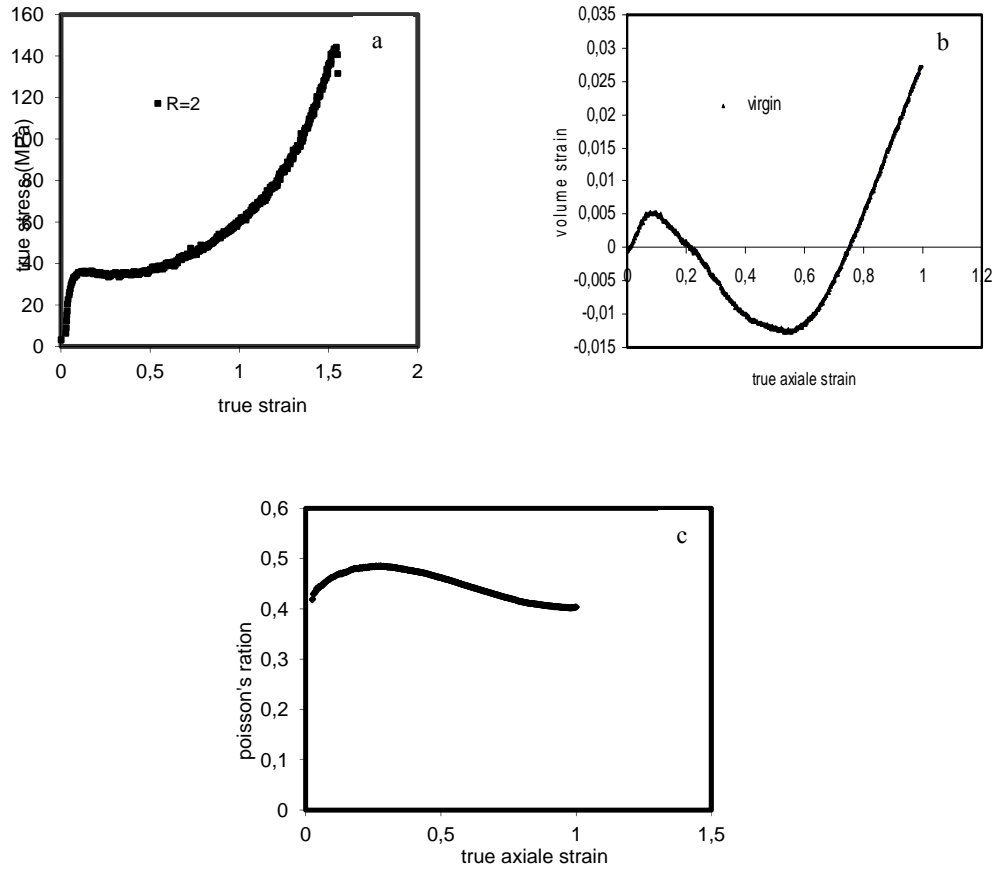

Fig.3: Mechanical behaviour of PE100: (a) true axial stress - true axial strain; (b) volume strain - true axial strain; (c) Poisson's ratio - true axial strain

Fig. 4 shows the influence of the notch radius on the behavior of the HDPE during the tensil tests. Indeed, the yield stress increases with the reduction of notch radius.
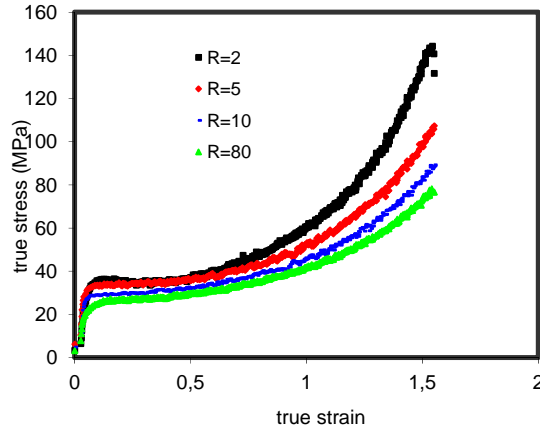
Fig.4. Radius effect on the mechanical behavior of HDPE

- **Creep test**

In the creep curves shown in Fig. 5 obtained at different fixed values of the stress, which are indicated in the figure for 1000 s at the strain rate of 5mm/min, at the first, an instantaneous deformation establishes, then primary creep commences. In this period, strain rate decreases because of strain hardening of the material, so that it causes the increase of material strength. After that, in the second stage, there is a secondary creep, the strain rate is minimum in this stage. At last, there is a fast creep or a period of tertiary or critical region, in which the fracture occurs. The figure also shows that increasing stress level increases the creep strain. All these viscous effects are related to delayed response of the polymer chains.
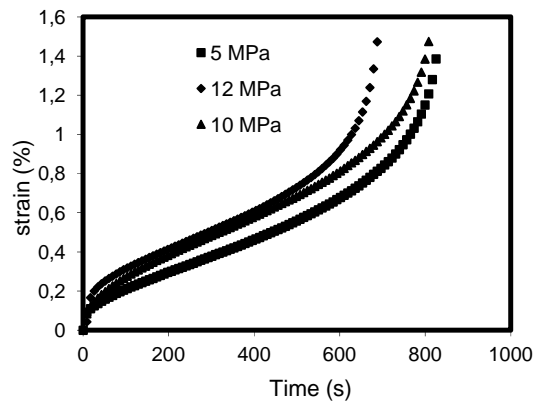

Fig. 5 Strain versus time curves in the creep experiments at three different stress levels at the strain rate of 5 mm/min.

- **Relaxation test**

Relaxation at the strain levels of 0,27 and 0.54 % at the strain rate of 5mm/min are performed for 1000 s in order to investigate the influences of the strain level on the relaxation behavior.

In metallic materials, relaxation at small strains is not significant. However, in polymeric materials at small strain level, relaxation is observed. Increasing strain level increases the stress drop. However, after reaching the flow stress, stress drop is not influenced by the strain level. Krempl and Khan (2003) [28] shown that stress drop during relaxation is independent of the strain level in the viscoplastic region. Stress versus time curves during relaxation are depicted in Fig. 6. We observed the decrease of lead from 350 N to 200 N after 1000s. These results exhibited the phenomena of viscoelastic relaxation.
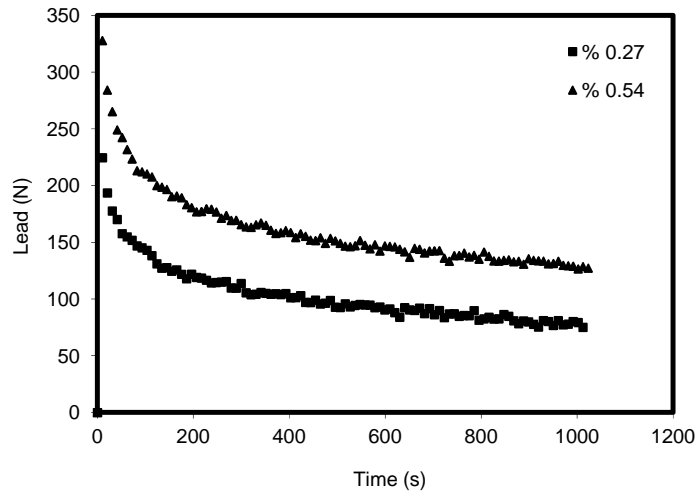

Fig. 6 Stress versus time curves during relaxation experiments at 0.27 and 0.54% strain levels

3.2 Annealing effect

3.2.1 Microstructure characterization

Melting temperature (T_m) and crystallinity degree, noted $\xi(t_h)$, obtained by Differential Scanning Calorimetry (DSC) for both virgin and annealed HDPE, for various hold time t_h , are done in table 1. It clearly appears that annealing process has as consequence the increasing of the melting temperature (T_m) and crystallinity degree $\xi(t_h)$.

Table 1
Melting temperatures and crystallinity degree of virgin and annealed PEHD for different hold time

Sample	Virgin	Aged 48h	Aged 96h	Aged 144h	Aged 192h
ΔH *melting enthalpy* (melting peak area)	131.6013 (j/g)	182.3488 (j/g)	200.1116 (j/g)	173.2895 j/g	171.2546 (j/g)
Melting peak	128.69 °C	130.15 °C	130.96 °C	130.75 °C	130.31 °C
Crystallinity degree	45.37 %	62.87%	69.04 %	61.75	60.75%

3.2.2 Annealing effect on mechanical behavior

In Fig. 7 we observe that most of the tensile properties of HDPE are affected by annealing. Indeed, significant changes in elastic modulus, yield stress and strain at break are noted. We note a drop of the yield stress from its initial value of 24 MPa before annealing to a value of 36MPa after annealing during 96h at 90°C, then the decrease of strain at break, after annealing.
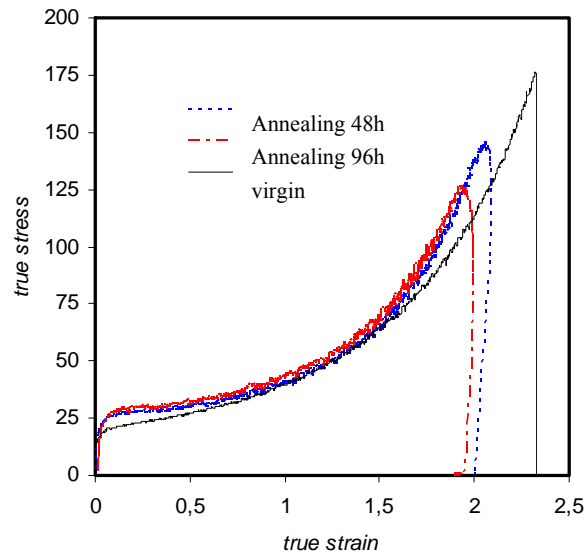

Fig.7: Annealing effect on mechanical behaviour of PE100 (true axial stress - true axial strain)

Fig. 8 shows the dependence of volume strain on axial strain. We note, in this figure, a rapid increase of volume strain for the HDPE annealed for 96 h. This increase is probably due to the formation and the growth of cavities. The formation of these cavities is favored in the case where the crystallinity degrees are important. This tendency is not the same for all the specimens tested. In the virgin HDPE, the dilatation is not important, because the preferred way of plastic strain is lamellae sliding and crystallographic slips initiated at yield [30]. Many studies have been performed also for years on rubber-toughened crystalline polymers but the issue, mainly involving rubber particles, was rather different. Here, microvoids are nucleated within the amorphous phase. In tension, cavitation starts in the amorphous layers between crystalline lamellae perpendicular to the stress axis. As the elongation of spherulites increases, cavitation spreads out progressively to more incline towards the stress axis amorphous layers. The cavitation is due to the "negative pressure" between crystallites lamellae, when they are separated by the applied stress [31].
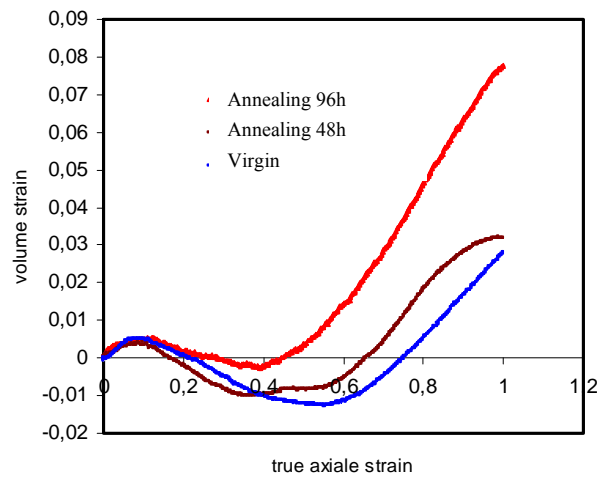

Fig. 7. Cavitation contribution to the volume change measured in dumbbell specimens after annealing

4. Conclusion

In this work, the annealing effect on HDPE responses was studied. Both experimental investigations are presented. Uniaxial tensile tests were conducted to investigate the annealing effects on HDPE behavior at large deformation. As a general observation, annealing leads to the increase in the mechanical properties. In particular, the increase in the yield stress and the maximal stress can be explained by the post-crystallization process. Differential scanning calorimetry

(DSC) technique supports an evolution of the morphology of HDPE. Indeed, an increase in the crystallinity degree has been quantified using DSC.

The results of the creep tests show that the creep strain increases with the stress levels. In the relaxation experiments, stress drop increases with the strain level. However, the stress drop is not sensitive to the strain level in the viscoplastic region.

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