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Abstract. — Mechanical behaviour of amorphous and semi-crystalline polyethylene terephthalate films is studied over five decades of strain rates, at temperatures below and above the glass transition. The data were obtained by combining measurements from conventional Instron machine with data from a high-speed tensile machine. The activation parameters are determined and compared with the activation process of the $\beta$ relaxation. Different modes of failure have been identified and the occurrence of an intermediate mode between ductile and brittle failure is shown. The brittle-ductile transition is estimated for each testing conditions and compared to the adiabatic-isothermal transition.

Résumé. — Le comportement mécanique du Poly(éthylène téréphthalate) amorphe et semi-cristallin est étudié sur plus de cinq ordres de grandeur de vitesses de déformation, de part et d’autre de la température de transition vitreuse. Les mesures expérimentales sont réalisées à l’aide d’une machine de traction Instron, pour les faibles vitesses de déformation, et d’une machine servo-hydraulique pour les grandes vitesses. Les paramètres d’activation sont déterminés et comparés à ceux de la relaxation secondaire basse température $\beta$. Différents modes de rupture sont identifiés ; entre une rupture typiquement ductile et une rupture fragile, un mode de rupture intermédiaire est mis en évidence. La transition ductile-fragile est estimée pour chaque condition d’essai, et comparée à la transition isotherme-adiabatique.

1. Introduction

All polymeric materials, amorphous or partially crystallized, show a mechanical behaviour (yield stress and strain, fracture energy...) very sensitive to microstructure and to the testing conditions such as temperature and strain rates. In order to understand the deformation process of polymers, the mechanical behaviour has to be studied over several decades of strain rates. Although such studies are very important in engineering design, few papers have been published on the high rate deformation testing [1–5].

Theoretical approaches have been proposed to model the mechanical behaviour of polymers, but these theories can be applied only in the case of homogeneous and isothermal deformations [6]. Meanwhile, firstly, a lot of polymeric materials show heterogeneous deformation such as necking or shear bands, secondly, since polymers are sensitive to the temperature change, it is

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expected that the heat developed during deformation will affect the stress-strain curves. Thus, for high strain rates, the thermal equilibrium of the material can not be obtained, involving adiabatic deformation.

Consequently, the theoretical analysis have to take into account both aspects: heterogeneous deformation and temperature changes leading to an adiabatic regime. For this purpose, a thorough knowledge of medium and high strain rates behaviour is required. Indeed it would help to compare the mode of deformation (homogeneous or heterogeneous) with the macroscopic mechanical properties and thus, to estimate the isothermal-adiabatic transition.

So this work concerns a study of the mechanical behaviour observed through tensile tests made on amorphous and semi-crystalline Poly(ethylene terephthalate) films over several decades of strain rates. The experimental activation parameters are determined by the Eyring’s rate analysis. A theoretical approach of the non-elastic deformation is proposed to understand the molecular mechanisms leading to high strain-rate plastic deformation. An investigation of the fracture surfaces is used to characterize the brittle-ductile transition. The adiabatic-isothermal transition is estimated and compared to the ductile-brittle transition.

2. Materials and Experimental Apparatus

2.1. MATERIALS. — Glassy films of PET have been produced by Rhône Poulenc Films Corporation. The thickness was about 870 μm and the average molecular weight 20 000 g mol⁻¹. The PET sheets were cut from a roll, annealed for 20 minutes at 363 K (10 K above the glass transition temperature) to be flattened and then cooled to room temperature. Dumbbell shape samples were cut with a LASER, to avoid cutting defects at the specimen border. After cutting, the material was annealed another 20 minutes at 363 K, to cancel the residual stress effects. Crystallinity ratio measurements with a gradient density column have proved that the quenched PET is really 100% amorphous.

Two different microstructures were obtained by isothermal crystallization at two different temperatures, 393 and 423 K in an uncontrolled atmosphere. These thermal treatments have given crystallinity ratios of 33 and 45% presenting two different microstructures: 33% corresponds to the maximum ratio obtained at the end of the primary crystallization process, 45% corresponds to the equilibrium ratio obtained at the end of the secondary crystallization process [7].

2.2. HIGH STRAIN RATES. — The high speed tensile tests were based on the servohydraulic Zwick ReI tensile apparatus. This machine has two operating modes: a servo controlled closed-loop mode for speeds between 0.01 ms⁻¹ and 0.5 ms⁻¹ and a valve with proportional opening for speeds from 0.5 to 20 ms⁻¹. The low part of the specimen was linked to a piston, which is accelerated progressively to the desired velocity, without contact with the specimen. The motion is transmitted to the specimen once the end of the track rod reaches a stop cup. This experimental procedure has two major consequences: (i) the high mass of the piston rod makes the amorphous specimen creep at high test temperatures, so, it was impossible to test amorphous PET at temperature above Tₐ; (ii) when the contact occurs and the motion is transmitted, the arm of the specimen oscillates, involving perturbations on the load signal. Thus, at high strain rates, the experimental results have to be filtered with a technique based on the fast Fourier transformation [4,8].

The position of the piston rod was measured by a capacity detector. The strain was deduced from the position of the piston. The load was measured by means of a load cell of 2 kN mounted in the fixture assembly and placed on the stationary side of the specimen.
2.3. **Low Strain Rates.** — The low strain rates were performed on an Instron 8165B tensile machine over the range of displacement speeds from $1 \times 10^{-6} \text{ ms}^{-1}$ to $6 \times 10^{-2} \text{ ms}^{-1}$. The load was measured with a load cell of 5 kN. The deformation was deduced from the cross head displacement.

To compare the stress measurements of both testing machines, we have studied the variation of the yield stress, with strain-rate, at room temperature given by both apparatus. No significant difference between the results given by these two testing methods was observed.

2.4. **Temperature Measurement and Control.** — The tensile tests were performed over the temperature range from 298 to 373 K. In all cases, the temperature was measured by two thermocouples, one next to the sample, the other one on a witness sample in the environmental chamber. All specimens were kept in the chamber during approximatively 2 minutes before testing, to be sure that the sample was in thermal equilibrium. This system allows temperature control with deviation lower than 1 K.

### 3. Results and Discussion

3.1. **General Features.** — The techniques described above have been applied to uniaxial tensile testing of PET at several temperatures. Load elongation curves were determined for temperatures of 298, 318 and 353 K for the amorphous PET, and 298, 323, 373 K for the semi-crystalline PET. In that case, it was possible to test crystallized material above its glass transition temperature without creep, thanks to the strengthening effect played by crystallites. All strain rates below $10^{-2} \text{s}^{-1}$ were achieved with the Instron testing machine and higher strain rates with the high speed tensile test machine. For each type of samples, the experimental results are the average of a minimum of 5 tests made at each strain rate.

The yield stress and strain were determined from the load extension curve, at the first maximum in load. Stresses were calculated from the reduced cross section area, assuming that the samples were deformed at constant volume. Deformations were deduced from the ratio $L/L_0$.

So true stresses and strains are derived from measurements via:

$$\varepsilon_\nu = \ln \left( \frac{L}{L_0} \right)$$

with:

$$\sigma_\nu = \frac{F}{S_0(1 - \nu \varepsilon_\nu)^2}$$

$L$, $L_0$, $S_0$ initial length, initial section of the sample, 
$\nu$ Poisson ratio taken as 0.5 (constant volume).

The strain rate was determined by the cross-head speed. But a constant displacement rate is not necessarily a constant strain rate. Until the yield stress, it was estimated that taking into account the strain, the error on the strain rate did not exceed 10%. After the yield stress, the deformation was often localized in a small volume because of the heterogeneous deformation. For low strain rates this volume is the volume of all the specimen, at medium strain rates, it coincides with the volume of the necked part of the sample. For high speeds, this volume concerns a smaller part of the specimen since it is reduced to about the shear band volume. So the local strain rate is much higher (about 2 to 5 decades) in that small volume than in the rest of the material [9].
3.2. RESULTS. — In Figures 1, 2 and 3, we can see respectively the influence of the strain rate, temperature and microstructure on the stress-strain curves of the PET. It appears that the yield stress behaviour is really influenced by these parameters. Figure 4 shows the yield stress as a function of the strain rate at various temperatures for the amorphous PET (Fig. 4a) and for the semi-crystalline PET (Fig. 4b). The yield stress presents a relatively high strain rate dependence. This type of behaviour allows to estimate the experimental activation parameters.

One of the experimental approaches to explore the molecular mechanism of the large deformations in solid polymers is the rate analysis. Most of these analysis intending to clarify the yield mechanism in polymers have been attempted mostly by Eyring or Ree-Eyring equations as theoretically grounded equations for the non linear viscosity [9–12]. Other approaches are based on thermodynamic analysis of the thermomechanically activated propagation of micro shears [13, 14].

These analysis lead to the equation:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp \left( \frac{-\Delta G}{kT} \right)$$

with

$$\Delta G = \Delta H_a - T \Delta S_a = \Delta H_0 - \sigma V_a - T \Delta S_a$$

\(\Delta H_a, \Delta S_a, V_a\) are enthalpy, entropy and volume activation parameters respectively, \(\Delta H_0\) is the height of the enthalpy barrier to cross by thermal activation.
Fig. 2. — Stress-strain curves showing the influence of the test temperature on amorphous PET at 298 K (Δ), 318 K (○), 353 K (○) for a strain rate of 8 s⁻¹.

Fig. 3. — Stress-strain curves showing the influence of the microstructure for a strain-rate of 8 s⁻¹. The test temperatures are chosen to test the specimen at constant $T_g - T$ of 30 K, for the 3 microstructures. (○) 45% crystallinity ratio, (Δ) 33% crystallinity ratio, (○) amorphous PET.
Fig. 4. — a) Evolution of the yield stress $\sigma_y/T$, in the case of amorphous PET for the three temperatures: 298 K (△), 318 K (◇), 353 K (○). b) Evolution of the yield stress $\sigma_y/T$, in the case of the semi-crystalline PET for various temperatures: for the 33% crystallinity ratio: 298 K (■), 323 K (□), 373 K (●), for the 45% crystallinity ratio: 323 K (◇), 373 K (▲).
In most usual studies, the stress sensitivity parameter:

\[ V_{exp} = kT \left( \frac{\partial \ln \dot{\varepsilon}}{\partial \sigma} \right) \text{, Structure} \]  

(3)

and the temperature sensitivity parameter

\[ \Delta H_{exp} = kT^2 \left( \frac{\partial \ln \dot{\varepsilon}}{\partial T} \right) \text{, structure} \]  

(4)

are actually measured. When (i) the microstructure remains unchanged (i.e. \( \varepsilon_0 \) is constant) and (ii) the molecular process is recognized as thermomechanically assisted jump over well identified energy barrier, we can write:

\[
V_{exp} = V_a \\
\Delta H_{exp} = \Delta H_a
\]

(5a)  

(5b)

Moreover, such an analysis has to be applied to the lower yield point, because at this stress, the material yields in a stationary state. However, when the deformation becomes heterogeneous, this stress and the corresponding strain are not related by law describing the local behaviour. Then, in this study, we have used the stress taken at the maximum of the stress-strain curve.

Thanks to the linear approximation (see Figs. 4), in accordance with Nanzai [15], \( V_{exp} \) can be obtained from the slope of the curve \( \frac{\sigma}{T} = f(\ln(\dot{\varepsilon})) \) for constant temperature. Thus, it appears that \( V_{exp} \) does not depend so much on strain-rate.

\( \Delta H_{exp} \) is estimated considering from equations (3) and (4) that:

\[
\Delta H_{exp} \approx -TV_{exp} \left( \frac{\partial \sigma}{\partial T} \right)
\]

(6)

\( \Delta H_{exp} \) is obtained for each strain-rate.

The experimental activation parameters are shown in Table I and represented in Figures 5a and 5b. Their probable evolution with temperature is schematically represented in dashed lines. As already shown by Nanzaï on PMMA [15], the experimental activation parameters reach their maximum near \( T_g \).
Table I. — Experimental activation parameters determined for the amorphous and semi-crystalline PET at various temperatures.

<table>
<thead>
<tr>
<th>microstructure</th>
<th>$T$(K)</th>
<th>$V_{exp}$(nm$^3$)</th>
<th>$\Delta H_{exp}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>amorphous</td>
<td>298</td>
<td>1.660</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>1.720</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>2.230</td>
<td>1.4</td>
</tr>
<tr>
<td>$X_c = 33%$</td>
<td>298</td>
<td>2.850</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>4.900</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>1.400</td>
<td>3.6</td>
</tr>
<tr>
<td>$X_c = 33%$</td>
<td>323</td>
<td>4.750</td>
<td></td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>1.780</td>
<td></td>
</tr>
</tbody>
</table>

These figures show the following points:

- When temperature increases, the experimental activation parameters increase for the amorphous and the semi-crystalline material. But after the glass transition temperature, they fall down quickly.

- Whatever the temperature, the experimental activation parameters of the semi-crystalline PET are higher than in the case of amorphous material.

- The semi-crystalline PET presents a greater temperature and stress sensitivity of the strain-rate.

Now, it seems interesting to compare the experimental results with the predictions given by theoretical approaches at least in the case of amorphous PET. This work uses an analysis proposed by Perez [16–18], who developed a molecular theory for the non-elastic deformation of amorphous polymers. In brief, this approach is based on (i) the existence of quasi-point defects corresponding to positive or negative nanofluctuations of specific volume, (ii) the hierarchically constrained nature of molecular dynamics. Under the application of a stress, some defects are activated into shear microdomains, which reversibly expand (anelastic strain) until they ultimately merge irreversibly with one another (viscoplastic strain).

To express the effect of combining mechanical bias and thermal energy on the mechanical response of polymers, Perez et al. [18] have proposed expressions relating the activation volume and enthalpy to the stress:

$$ V_\alpha = \frac{3U_\beta}{2\sigma_0} \left(1 - \frac{\sigma}{\sigma_0}\right)^{1/2} $$

$$ \Delta H_\alpha = U_\beta \left(1 - \frac{\sigma}{\sigma_0}\right)^{3/2} $$

with $U_\beta$: the energy of the $\beta$ relaxation, $\sigma_0$: the shear stress that would be required for plastic deformation at 0 K ($\sigma_0 = G/2\pi = 350$ MPa for amorphous PET).

At low temperature, the activation of plasticity needs very high stresses, so $V_\alpha$ and $\Delta H_\alpha$ decrease and when the applied stress increases toward $\sigma_0$, $V_\alpha$ and $\Delta H_\alpha$ equal zero. When temperature is increased, the flow regime results from a balance between disorder created by nucleation and expansion of shear microdomains and its diminution via structural relaxation.
Fig. 5. — a) Evolution of the apparent activation volume versus temperature for amorphous PET (†), for 33% crystallinity ratio (▲), and for 45% crystallinity ratio (△). (---) represents the experimental evolution of $V_{\text{exp}}$ (the trends are deduced from Ref. [15]), (—) represents $V_{\text{exp}}$ deduced from the molecular model [16–18]. b) Evolution of the apparent activation energy versus temperature at various strain-rates. For amorphous PET (x) 2.4 s$^{-1}$, (+) 7.8 s$^{-1}$, (●) 20 s$^{-1}$, (◇) 40 s$^{-1}$, for 33% crystallized PET with (♠) 0.01 s$^{-1}$, (■) 0.1 s$^{-1}$, (△) 1 s$^{-1}$, (---) represents the experimental evolution of $\Delta H_{\exp}$ (the trends are deduced from Ref. [15]). (—) represents $\Delta H_{\exp}$ deduced from the molecular model [16,18].
thus leading to a stationary quasi point defects concentration depending on temperature. Such a theory allowed to obtain calculated $\sigma - \varepsilon$ curves in agreement with experimental results (see Refs. [16–18]). As described in reference [18], this approach can be used to estimate the temperature evolution of the experimental activation enthalpy and volume. The calculated evolution of $V_{\text{exp}}$ and $\Delta H_{\text{exp}}$ are plotted in Figures 5a and b, and are in fair agreement with those obtained experimentally.

The evolution of the calculated activation parameters exhibits a linear behaviour for temperature lower than about 200 K. From 300 K, the experimental activation parameters $V_{\text{exp}}$ and $\Delta H_{\text{exp}}$ show the same evolution as $V_a$ and $\Delta H_a$, thus verifying relations (5). But for higher temperatures, $V_{\text{exp}}$ and $\Delta H_{\text{exp}}$ increase more and more, becoming much higher than the theoretical prediction of $V_a$ and $\Delta H_a$. In that case, relations (5) are not valid, implying some variation in microstructure when temperature of mechanical test is increased, as mentioned by Escaig [14] in his thermodynamic analysis of plasticity.

To sum up, let us notice that the molecular model recalled in this work takes into account the change of structure involved during mechanical test. Then it is capable to reproduce the experimental variation of the activation parameters with temperature from the lowest temperatures, to near $T_g$.

Moreover, the results of Figures 5 involve the following question: what is the role played by the crystalline phase comparatively to the amorphous phase in the mechanical response? Below $T_g$, in annealed PET, the crystalline lamellae reduce the chain mobility of the amorphous phase, so the molecular motion should be more constrained. This effect only involves an horizontal shift of the activation parameters along the temperature axis. In fact, it cannot explain the high values of the activation parameters obtained in the semi-crystalline PET. Consequently, these results suggest that the change in behaviour is due to the presence of crystallites in the material, which could play a role in the deformation mechanism of the polymer.

For high strain rates, the mechanical behaviour and the mode of deformation change, because of the occurrence of adiabatic regime and brittle failure. In the next two parts, we will try to characterize the change of deformation mode with strain rate, in order to estimate when the regime becomes adiabatic. For that purpose, we need first to determine exactly the strain rate for which the material becomes brittle.

4. Ductile-Brittle Transition

The ductile-brittle transition has been explained assuming that brittle fracture and plastic deformation are independent processes, having a different temperature dependence [19,20]. For instance, brittle stress is not so much affected by strain-rate, contrary to the yield stress. Consequently, the experimental ductile-brittle transition conditions are sensitive to the temperature of the test, to the strain-rate, to the microstructure (molecular weight, annealing, crystallinity) and also to the shape of the specimen [21].

Some authors have proposed that the ductile-brittle transition may be associated with the primary or secondary mechanical relaxation [22]. Many polymers are ductile below the $\alpha$ relaxation temperature; in this case, it is sometimes possible to relate the ductile-brittle transition to the low temperature relaxation. But this hypothesis has no general validity, because the brittle-ductile transition occurs at fairly high stresses, whereas, the dynamic mechanical behaviour is measured in the linear stress-strain region.

The distinction between brittle and ductile failure is also manifested in 2 ways:

- The rupture energy, which is important for practical applications.
- The nature of the rupture surface.
Table II. — *Brittle-ductile strain-rates for the amorphous and semi-crystalline PET.* The inflexion point of the curve rupture energy versus the strain-rate characterizes the position of the transition.

<table>
<thead>
<tr>
<th>microstructure</th>
<th>( T(K) )</th>
<th>( \dot{\varepsilon}_{DB}(s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>amorphous</td>
<td>298</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>100</td>
</tr>
<tr>
<td>( X_e = 33% )</td>
<td>298</td>
<td>( \dot{\varepsilon}_{DB} &lt; 10^{-3} )</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>( \dot{\varepsilon}_{DB} &gt; 10^{-1} )</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>( 10 &lt; \dot{\varepsilon}_{DB} &lt; 100 )</td>
</tr>
<tr>
<td>( X_e = 45% )</td>
<td>323</td>
<td>( 10^{-1} &lt; \dot{\varepsilon}_{DB} &lt; 1 )</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>( 10 &lt; \dot{\varepsilon}_{DB} &lt; 100 )</td>
</tr>
</tbody>
</table>

4.1. Rupture Energy. — The rupture energy is defined by the relation:

\[
W = \int_0^{\varepsilon_f} \sigma d\varepsilon
\]  

(8)

So that, \( W \) is determined by measuring the area beneath the experimental stress strain curve.

The rupture energy versus strain rate is shown in Figure 6a for the amorphous PET at room temperature and in Figure 6b for the semi-crystalline PET at various temperatures. The other curves obtained at higher temperature for the amorphous PET are not represented because of the scatter of the results. Nevertheless, the same trends, as for the polymer tested at room temperature, were found. Two different transitions appear: at low and very high strain rates. For the other microstructures the same transitions exist certainly, but the strain rate range is too small to see the first transition (Fig. 6b). For the semi-crystalline PET tested at 373 K both transitions seem to be superimposed.

The strain rate, \( \dot{\varepsilon}_{DB} \) at which the ductile-brittle transition takes place is indicated in Table II. The value of \( \dot{\varepsilon}_{DB} \) is taken at the inflexion point of the high strain rate transition. The brittle failure shows considerable scatter in the value of the rupture energy. So the temperature dependence of the ductile-brittle transition does not appear clearly below the glass transition temperature. In the opposite, above the glass transition, the strain rate at which the ductile-brittle transition occurs increases by 3 to 4 decades. Thus, the microstructure has a great influence on the ductile-brittle transition, the crystallites increase the strength of the material, but decrease really the ductility.

4.2. Rupture Surfaces. — The rupture surface observation can also yield an indication of the distinction between the brittle and ductile failure. A set of photos of the specimen was done for various strain rates and showing different modes of failure. We found five different types of rupture in the amorphous PET tested at 298 K, over the range of strain rates. At low strain rate, the specimen exhibits uniform deformation. When \( \varepsilon \) increases, the deformation is localized in a neck and the sample cold draws until its natural draw ratio (Fig. 7). In all cases, the heterogeneous deformation is initiated by shear banding. At higher strain rates, the ductile rupture takes place for medium deformation ratios (Fig. 8); the polymer yields in a well defined deformation band before rupture (Fig. 9).
For higher strain rates (Fig. 10a), the brittle fracture is initiated near the border of the specimen. But the rupture plane deviates at 45° of the stress axis. The same type of crack deviation was observed by Takemori [23] in traction/compression fatigue tests on unnotched specimens of PC and by Kastelic [24], and was due to shear bands. An analysis based on
SEM shows two distinct regions on the rupture surface. Close to the border of the sample, the rupture surface is a mirror (Fig. 10b). When we focused on the mist region (Fig. 10c), we can see that deformation takes place by shearing. Steps are visible with planes making an angle of approximately 45°, with the stress axis. So, we assume that deformation takes place by shearing, inside shear bands. The width of these shear bands corresponds to the height of the steps. We suggest that failure follows the planes of shear bands, going through it and thus, creating a step. In compressed samples of PS, Chau et al. [25] found the same type of rupture with steps following shear bands. We can suppose that failure occurs as shown in Figure 11. In this type of failure, the macroscopic characteristics (rupture stress, strain) seem like brittle fracture, but the SEM investigation proves that it is ductile. At still higher strain rates, brittle failure is obtained with fracture planes perpendicular to the stress axis (Fig. 12). This type of fracture starts from a surface defect. So the observations confirm that the brittle-ductile transition occurs in the strain rate range between 50 and 200 s\(^{-1}\).

Even if it is assumed that the brittle fracture and plastic flow are independent processes, the SEM observations show an intermediate stage between the fully ductile failure and the fully brittle one: this stage is characterized by the "mist" mode of failure involving small macroscopic plastic shear deformation.
5. Isothermal-Adiabatic Transition

The previous observations have shown that plastic deformation takes place by shear banding for strain rates greater than $10^{-2}$ s$^{-1}$ (value for the amorphous PET at 298 K). The higher is the strain rate, the smaller is the volume concerned by the deformation. As a consequence, when the strain-rate increases, there are only small parts of the sample concerned by deformation. So, it is possible that the heat produced by mechanical work cannot be conducted away rapidly enough, involving adiabatic conditions. In adiabatic deformation, the temperature rise affects a small volume, the temperature gradient reaches high values. In that case, the strain hardening is prevented and the specimen fails in a ductile manner.

So it seems interesting to estimate first of all, the temperature rise when deformation becomes heterogeneous and then, the strain rate corresponding to the isothermal-adiabatic transition.

By employing the first law of thermodynamics, we have:

$$W = \Delta U + Q$$  \hspace{1cm} (9)

$\Delta U$ is the change of internal energy, due to changes of conformation and defects creation, $Q$ is the heat dissipated in the material, $W$ is the mechanical work. During non-elastic deformation, a part of the mechanical work is stored as internal energy. Oleinik [26] found for PET an amount of 15% of the mechanical work stored in the sample at yield point. The energy stored in the material is small, so we neglect it in relation (9).

The mechanical work is given by the relation (8). We use the following approximation to estimate $W$, because, considering that all deformation takes place inside shear bands with a deformation ratio of 2 [27], the elastic part of the work can be neglected.

$$W = \sigma \varepsilon$$  \hspace{1cm} (10)

An expression for the temperature rise during the extension of the specimen can be developed. The temperature variation is then given by

$$\Delta T = \frac{W}{\rho C_p}$$  \hspace{1cm} (11)

with $C_p = 1550$ J K$^{-1}$kg$^{-1}$. heat capacity, $\rho = 1420$ kg m$^{-3}$. specific weight [28].
Fig. 10. — a) Mode of rupture of the amorphous PET tested at 298 K for a strain rate of 10 s\(^{-1}\). b) Scanning electron microscopy observation in the cut border of the sample: failure seems like a mirror. c) Scanning electron microscopy observation in the “mist” zone of the sample. Small plastic deformation is visible, taking place by shearing.
Fig. 11. — Schematic failure of a sample showing the 2 modes of failure. a) The initial crack begins with a defect on the cut border of the sample, then it deviates from the horizontal plane to 45° of the stress axis, following a shear band. b) The intersections with other shear bands nucleated during the process create steps on the rupture surface. Only one step is represented here, considering that two shear bands developed during rupture.

Fig. 12. — Mode of failure of the amorphous PET tested at 298 K for a strain rate of $10^2$ s$^{-1}$

Considering the shear yield stress is 35 MPa, a temperature increase of 35 K occurs in the shear band. We have verified the temperature rise developed during necking, with a thermocouple embedded in the specimen. The temperature increase when the shoulder of the neck goes in front of the thermocouple was 38 K. This is in agreement with the results found by infrared camera or by thermosensitive films [1,29,30].

Now it seems interesting to estimate the strain rate of the isothermal-adiabatic transition. The characteristic distance, $x$, the heat can diffuse has to be compared to the size of shear bands. In other words, if the heat diffuses outside of the shear band, we can consider that the deformation is isothermal (Fig. 13a). But if the strain-rate is high enough, heat cannot diffuse outside of the band, deformation becomes adiabatic (Fig. 13b). Let us assume the conditions will be really isothermal if the temperature increase due to deformation will not exceed 1 K.
Fig. 13. — Criterion for the isothermal-adiabatic transition. The distance over which heat can diffuse is called \( x \); when \( x \) is greater than the thickness of the band \( e_{sb} \), then deformation is isothermal a). If \( x \) is smaller than the thickness of the shear band \( d_{sb} \), then deformation is adiabatic b). The \( Y \)-axis represents the temperature variation.

So we choose the following criteria:

- if \( x > 5 \, e_{sb} \): conditions can be admitted isothermal, because the temperature rise will be less than 1 K,
- if \( x < 5 \, e_{sb} \): conditions become adiabatic.
- for \( x = 5 \, e_{sb} \): the conditions are between isothermal and adiabatic, a temperature rise is visible.

with \( x \): mean distance for heat diffusion and \( e_{sb} \): shear band thickness. The SEM investigations of shear bands have shown thicknesses of approximately 10 \( \mu \)m.

The characteristic distance heat can diffuse in a time \( t \) is \((\alpha t)^{0.5}\), where \( \alpha \) is the thermal diffusivity, which in turns equals \( \frac{K}{\rho C_p} \). \( K \) is the thermal conductivity \((K = 0.22 \text{ W m}^{-1}\text{K}^{-1}\) [28]).

Using \( x = 5 \, e_{sb} \), we can estimate the time associated to the heat diffusion:

\[
 t = \frac{x^2}{\alpha} \quad (12)
\]

This time corresponds to the time necessary for deformation to occur inside a shear band. \( t \) is macroscopically given by:

\[
 t = \frac{\Delta L}{V_t} \quad (13a)
\]

\[
 V_t = \dot{\epsilon} L_0 \quad (13b)
\]

\( V_t \) is the cross head speed, \( \Delta L \) is the change in specimen length during the test. If the deformation is localized in shear bands, we can write:

\[
 \Delta L = N e_{sb} e_{sb} \quad (14)
\]
$N$ is the number of shear bands and $\varepsilon_{sb}$ the deformation inside the shear band. The distance between shear bands is then given by:

$$d_{sb} = \frac{L_0}{N}$$  \hspace{1cm} (15)

Combining equation (13), (14) and (15) one has:

$$t = \frac{\varepsilon_{sb} \varepsilon_{sb}}{d_{sb} \dot{\varepsilon}}$$  \hspace{1cm} (16)

In a tensile test, several bands form. But when the deformation becomes adiabatic, the first band which propagates through the specimen leads to failure. So, here, the calculation concerns the first shear band formed in the specimen. Consequently, we can write that $N = 1$, implying that the distance $d_{sb}$ equals $L_0$. Relation (16) leads to:

$$t = \frac{\varepsilon_{sb} \varepsilon_{sb}}{\dot{\varepsilon} L_0}$$  \hspace{1cm} (17)

Let us recall that $L_0 = 50$ mm is the initial length of the sample, and $\dot{\varepsilon}$ is the overall strain rate. Such a time has to be compared to that deduced from equation (12). So that the condition for isothermal-adiabatic transition is

$$\frac{\varepsilon_{sb} \varepsilon_{sb}}{\dot{\varepsilon} L_0} \approx \frac{(25\varepsilon_{sb}^2)}{\alpha}$$  \hspace{1cm} (18)

So the strain rate for which the isothermal deformation becomes adiabatic is given by:

$$\dot{\varepsilon} \approx \frac{\varepsilon_{sb} \alpha}{25\varepsilon_{sb} L_0} \quad \text{or} \quad V_t = \frac{\varepsilon_{sb} \alpha}{25\varepsilon_{sb}}$$  \hspace{1cm} (19)

For amorphous PET tested at 298 K, the strain rate of the isothermal-adiabatic transition is $2 \times 10^{-2}$ s$^{-1}$. This transition coincides with the abrupt change of the rupture energy observed at low strain rates.

To sum up, the rupture energy shows two drops: that observed at low strain rates could result from the isothermal-adiabatic transition, and the one occurring a few decades of strain rates higher could be the consequence of the ductile-brittle transition (Fig. 6a). We can suppose that difference of strain rates between both transitions is due to the high temperature rise inside the shear band involving strain softening. For high strain rates, failure is initiated in a brittle manner, but the crack deviates at $45^\circ$, to give ductile deformation. We can think that the temperature rise in the shear bands increases the molecular mobility, and makes the plastic deformation easier. When the strain-rate is too high, the time allowed to the deformation is too short and the brittle failure takes place in the elastic part of the stress-strain curve.

6. Conclusion

The mechanical behaviour of amorphous and semi-crystalline PET has been studied from quasi-static conditions to high strain-rates. Analysis of the activation parameters of high strain-rate mechanical behaviour has confirmed non-elastic deformation involved structural changes during the test. The examination of rupture surfaces has revealed firstly the important role played by shear bands in the deformation process, secondly, the existence of an intermediate stage between the brittle failure and ductile failure, implying micro shear strain.

The evolution of rupture energy versus strain rate has shown two drops. At low strain rates, the first change was due to isothermal-adiabatic transition. At higher strain rates, the second drop is due to the ductile-brittle transition.
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References


