Viscoelastic behaviour of thin bioriented poly(ethylene terephthalate) films under low and medium stresses

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A theoretical model is proposed in order to explain the mechanical behaviour of thin bioriented poly(ethylene terephthalate) (PET) films at low and medium stresses. This investigation requires one to introduce a theory of deformation of amorphous PET and coupling of the behaviour laws of the two phases (crystalline and amorphous). A newly developed molecular model of non-elastic deformation of glassy solids based on hierarchical constrained molecular movements and activation of defects is used and extended to the non-linear behaviour of the creep compliance function. Creep tests are carried out at low and medium stresses on amorphous and semicrystalline films in order to study (i) the linear domain, (ii) the transition to non-linear behaviour of the compliance (defined by some critical stress, σ_c) and (iii) the qualitative evolution of the creep compliance beyond this critical stress value. Semiquantitative agreement is found between theoretical predictions and experimental data in a large domain of stresses including the critical value σ_c. By assuming in a first step that partially crystalline films are two-phase systems, their mechanical behaviour can be explained by coupling an amorphous and a crystalline phase following Takayanagi's model. In this coupling, the crystalline phase can be considered as a perfect crystal with a Young's elastic modulus in the in-plane direction of about $E_{c\parallel} \approx 110$ GPa. In a second step, the mechanical response of the amorphous phase of biaxially oriented thin PET films is compared with that of bulk amorphous PET. We find that these two behaviours are very different, first because of an important reduction of 'defect' concentration in the amorphous phase of thin biaxially oriented PET films and secondly because of an increase of relaxation characteristic time due to the proximity of crystallites.

(Keywords: poly(ethylene terephthalate); semicrystalline polymer; creep; non-linear behaviour)

INTRODUCTION

Poly(ethylene terephthalate) (PET) has many important commercial applications: as a mono-oriented fibre, it is used in textiles and, as a biaxially oriented film, it is used as a substrate for flexible magnetic recording media (tapes and floppy discs) and also for packaging or graphic arts. PET film is industrially produced by extrusion of a polymer that is quenched and then biaxially stretched. Mechanical stretching of these films, induces partial crystallinity. These biaxially oriented films can be looked at as a composite material exhibiting an amorphous and a crystalline phase.

The study of the mechanical properties of these films implies a good knowledge of (i) the physical and mechanical properties of each polymer phase and (ii) the geometrical distribution of these two phases. For that purpose, creep tests were applied to both totally amorphous and partially crystalline PET films. The critical stress above which a non-linear component exists in the creep function was specially studied for the totally amorphous and semicrystalline films between ambient temperature and the glass transition temperature.

The aim of the present paper is to model the mechanical response of semicrystalline polymers in terms of separate crystalline and amorphous phases. A coupling model based on phenomenological concepts previously developed is introduced.

The deformation of the amorphous region can be analysed with a molecular model previously presented and based on (i) the mobility of defects as developed in physical metallurgy and (ii) the concept of a hierarchical correlation. But further developments are introduced in order to take into account the non-linear component in the creep compliance function through a global formulation including a large range of stress values. Moreover, in the present work, the mechanical response of the amorphous region of biaxially oriented PET films is extracted and compared with the mechanical response of the bulk amorphous phase.

MATERIALS AND EXPERIMENTAL METHODS

The films were produced by Rhône-Poulenc Films. The samples are cut from a PET roll so that one optical orientation axis (0°) corresponds to the extrusion direction. The amorphous sample is 850 μm thick and

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the semicrystalline and biaxially oriented ones are 75 μm thick. All the samples are 5–15 mm wide and 20–70 mm long.

The level of crystallinity of the biaxially oriented films as measured by small-angle X-ray scattering techniques ranges between 40 and 50%.

There is no physical ageing of the roll before creep tests because it was stored at low temperature. All the tests were conducted at constant relative humidity. Creep tests were performed with an Adamel Lhomargy MF-11 apparatus modified in order to work at low load (range: 0–50 N) and low displacement (range: 0–1 mm).

The stress is applied to the sample with an electromagnetic system and controlled by a computer and a D/A–A/D converter. The strain is measured with two capacitive sensors and analysed by the same computer. In the present work, stress ranges between 5 and 80 MPa, deformation between 1 and 4%, temperature between 46 and 77°C and creep time between 10 and 40 min.

EXPERIMENTAL RESULTS

The elastic Young's moduli of the amorphous PET sample are assumed to have the same value in all directions (isotropy), i.e. $E_a \approx 2$ GPa, as measured in the longitudinal direction. The corresponding value of the elastic Young's modulus for biaxially oriented PET films is $E_{sc\parallel} \approx 4.7$ GPa (measured in the longitudinal direction). An example of a series of creep tests carried out on thin biaxially oriented films is shown in *Figures 1a* and *1b* for two temperatures. All the creep tests of each series are carried out on the same sample in ascending stress order (with a recovery time equal to three times the creep one) so that the physical state of the material is not disturbed.

The general shape of the creep curves $J_\sigma(t)$ for various values of the applied stress σ at constant temperature shows that two distinct domains exist: (i) Below some critical value σ_c of the stress, the creep curves are very close to one another and become the same at the end of recovery. This means that the anelastic component depends slightly on the stress σ in the linear domain. (ii) Above this yield value σ_c, the creep curves are strongly dependent on applied stress σ, even after recovery.

The critical stress σ_c is defined as follows:

$$\sigma_c = \frac{J_{\sigma=\sigma_c}(t_f) - J_{\sigma=0}(t_f)}{J_{\sigma=0}(t_f)} > 10\% \qquad (1)$$

where t_f denotes the creep time. In fact, σ_c is nearly independent of t_f. Different values of the critical stress σ_c are displayed in *Table 1* for both the amorphous and semicrystalline films. These values are obtained within a few megapascals, which is accurate enough to deduce tendencies and make comparisons.

Figure 1c represents two creep curves obtained with the amorphous and semicrystalline films, with the same conditions (temperature, stress, ...) and in both cases in the linear domain ($\sigma < [\sigma_c(T)]_a$ and $\sigma < [\sigma_c(T)]_{sc}$). The following comments can be made:

(i) Young's modulus is higher for the semicrystalline film than for the amorphous one, $E_{sc} > E_a$.

(ii) The creep curve for the semicrystalline film is often below that for the amorphous film, $[J_\sigma(t)]_a > [J_\sigma(t)]_{sc}$, which corresponds to a smaller deformation under the same stress σ.

(iii) The critical stress is higher (at the same temperature) for the semicrystalline film, $[\sigma_c(T)]_{sc} > [\sigma_c(T)]_a$.

(iv) The total loss of mechanical behaviour occurs at higher temperature.

These results can be explained by the existence of a crystalline phase within biaxially oriented films. As the crystalline phase has a Young's modulus higher than the amorphous phase, it makes the material stiffer. In addition, the glass temperature of the amorphous phase is higher than that of the amorphous bulk material. All these results are in full agreement with the literature[1–4].

Finally, the critical stress σ_c seems to be a decreasing function of temperature for the two cases (bulk amorphous and semicrystalline).

CASE OF TOTALLY AMORPHOUS PET

In order to analyse quantitatively the creep compliance curves of this material, we suggest using the non-elastic deformation model of glassy solids introduced earlier[5–8] and able to explain the mechanical behaviour of amorphous PET even in the non-linear domain.

The creep compliance function contains three components: elastic, anelastic and viscoplastic. (i) The first one is simply equal to $J_{elas} = 1/E_a$ where E_a is the elastic Young's modulus. (ii) The two others, J_{anel} and J_{visc}, will be specified by the model developed here. We present only the basic hypotheses and the physical meaning of the different parameters.

The amorphous polymer is described in terms of a close packing in which there are randomly distributed sites corresponding to density microfluctuations, which will be called 'defects'. For $T > T_g$, these sites are continuously redistributed due to thermal fluctuations (Brownian motion), but they are 'frozen' for $T < T_g$.

The application of a macroscopic stress results in microstructural rearrangements around the defects where resistance is significantly weaker than in the rest of the material, introducing a shear. The shear of the defects implies formation of *shear microdomains* (hereafter called SMD). As long as this shear remains located around the defects, the expansion of the deformation is reversible (corresponding to recovery behaviour).

We expect the characteristic time τ_β of excitation of the defects and nucleation of the SMD to have an Arrhenius temperature dependence:

$$\tau_\beta = \tau_0 \exp(U_\beta/kT) \qquad (2)$$

where U_β represents the height of the energy barrier that must be overcome by thermal activation and τ_0 is the inverse of the Debye frequency ($\tau_0 \approx 10^{-13}$ s).

In *Figure 2a* are plotted the two equilibrium configurations, called A and C, of the system. The transition from A to C requires overcoming an energy barrier U_β (unstable state B).

Taking the derivative of the energy function $U(x)$, a new diagram is obtained in terms of the force $F(x) = \mathrm{d}U(x)\,\mathrm{d}x$. The energy required to reach U_β is obviously defined by:

$$U_\beta(\sigma = 0) = \int_{A}^{B} [F(x) - F(A)]\,\mathrm{d}x \qquad (3)$$

This value $U_\beta(\sigma = 0)$ corresponds to the dotted area in *Figure 2b*.

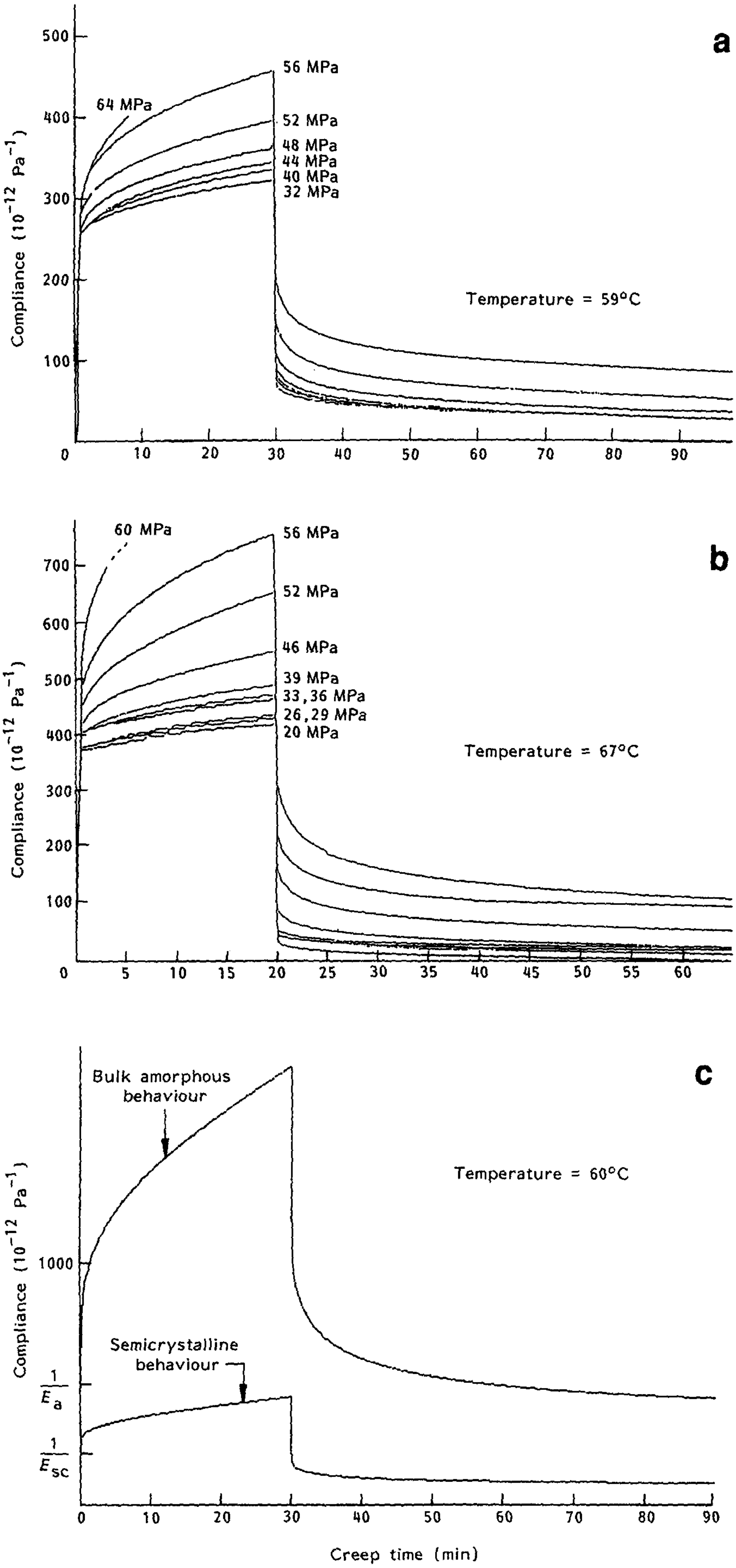

Figure 1 (a), (b) Evolution of creep compliance curves for biaxially oriented film under constant applied stress (in ascending order) for two temperatures: (a) 59°C and (b) 67°C. (c) Comparison between biaxially oriented film and bulk amorphous creep behaviour in the same conditions (linear domain)

Table 1 Dependence of critical stress on temperature

	Critical stress, σ_c (MPa)	
Temperature (°C)	Amorphous	Bioriented
46	25	55
59	10	45
67		37
77		32

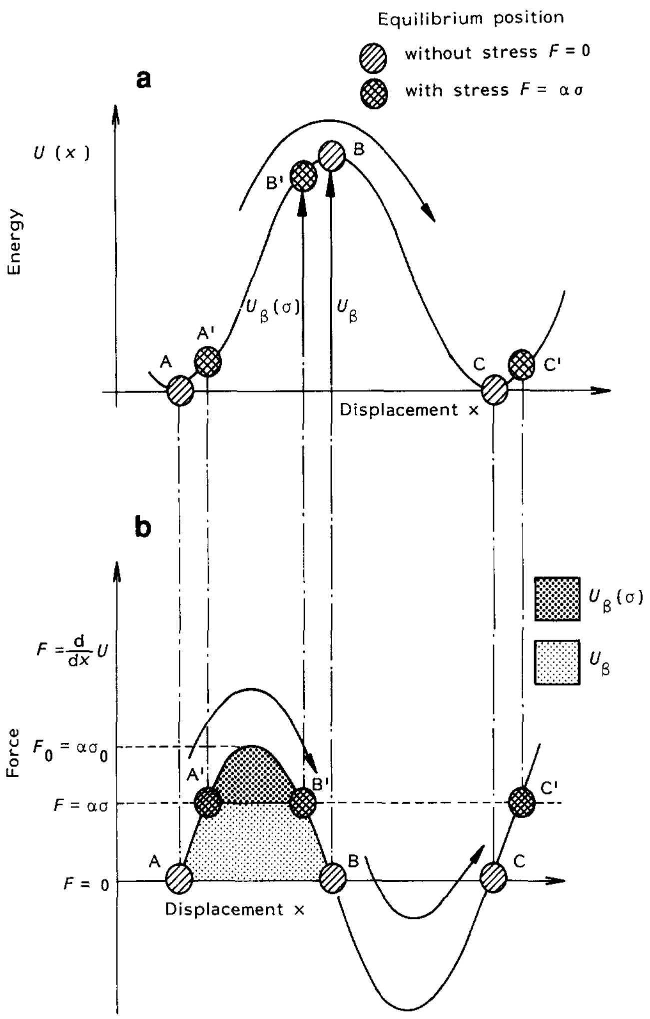

Figure 2 Diagram of energy (a) and force (b) during a configurational change between different equilibrium states (*A*, *C* without any stresses and *A'*, *C'* under a stress σ)

Under the action of a stress σ, the initial equilibrium position (A, B and C), as defined on *Figure 2b* by $F(\mathrm{A}) = F(\mathrm{B}) = F(\mathrm{C}) = 0$, is moved slightly to a new state (called A', B' and C') defined by an equilibrium force proportional to the applied stress: $F(\mathrm{A'}) = F(\mathrm{B'}) = F(\mathrm{C'}) = \alpha\sigma$. This gap between these two equilibrium positions (A, B, C and A', B', C') corresponds to the internal response of the material to the external stress σ. In this new configuration, the transition from state A' to state C' via B' requires a new level of energy $U_\beta(\sigma)$ defined by:

$$U_\beta(\sigma) = \int_{\mathrm{A'}}^{\mathrm{B'}} [F(x) - F(\mathrm{A'})]\,\mathrm{d}x \tag{4}$$

This value $U_\beta(\sigma)$ corresponds to the hatched area in *Figure 2b*.

If F is expected to have a parabolic shape between A and B with a maximum value equal to $\alpha\sigma_0$, this relation between $U_\beta(\sigma)$ and U_β becomes:

$$U_\beta(\sigma) = U_\beta(1 - \sigma/\sigma_0)^{3/2} \tag{5}$$

Physically, stress σ_0 corresponds to the removal of the energy barrier, i.e. the threshold of creation of a totally irreversible shear deformation without any thermal activity (0 K).

Frenkel[9], in a model based on the packing of perfect spheres and extrapolated to the atomic level of mechanics of continuous domain laws, estimates this value σ_0 to $G/2\pi$, where G is the elastic shear modulus at temperature 0 K. In this case, the thermally activated overcoming of the energy barrier U_β is stress-assisted, which leads to the concept of 'thermo-mechanical activation'.

When the application time of the stress is long enough, diffusional rearrangement occurs around SMD, inducing their expansion. The deformation remains anelastic because the elastic energy associated with SMD implies their reversible constriction after removal of the applied stress. Thus, the SMD will be stretched out as long as their borders are in contact. This phenomenon corresponds to annihilation of elastic energy accumulated all along lines bordering SMD, and thus induces an irreversible macroscopic deformation (viscoplastic flow).

The SMD have correlated expansions in the way that a chain movement requires previous molecular movements leading to a special configuration allowing motion to occur. For example, in polymer systems, long-distance movements are not possible without taking into account interactions between all the segments of macromolecular chains.

When the application time of the stress increases, the long-distance movement of a segment requires overall movement of the different parts of the macromolecular chain. In this sense, entanglement nodes, chemical or physical reticulation points such as crystalline strips in semicrystalline polymers, behave as diffusion obstacles and thus increase correlation effects[7]. Quantitatively, these correlation effects are incorporated in the present model through parameter χ, which characterizes the efficiency of correlation effects between elementary molecular movements.

SMD expansion is achieved on a timescale between $t = \tau_\beta$ and $t = \tau_{\max}$ with a characteristic time given by[6]:

$$\tau(t) = \tau_\beta(t/t_0)^{1-\chi} \tag{6}$$

Time t_0 characterizes the timescale of molecular rearrangements: $t_0 \approx 10^{-6}$ s. The limit value of time $\tau(t)$ can be specified by assuming the cut-off $\tau_{\max} = \tau(\tau_{\max})$ leading to the following value:

$$\tau_{\max} = (\tau_\beta/t_0^{1-\chi})^{1/\chi} \tag{7}$$

There are two ways to take into account the distribution of the characteristic times between τ_β and $\tau_{\max}$:

(i) By using a stretched exponential function able to approximate this distribution of characteristic times. Integration of the evolution law of the equilibrium position between $t = \tau_\beta$ and $t = \tau_{\max}$ gives:

$$J_{\mathrm{anel}}(t) = A\left\{1 - \exp\left[-\left(\frac{t}{\langle\tau\rangle}\right)^{\chi}\right]\right\} \qquad \langle\tau\rangle = \left(\frac{\chi\tau_\beta}{t_0^{1-\chi}}\right)^{1/\chi} \tag{8}$$

(ii) By introducing directly a distribution in J_{anel}. It is assumed that the distribution is Gaussian with an average value $< \tau > = \tau_{\max}$ and a standard deviation given by $B = B_0(1 + T_1/T)$. An experimental study[10] of creep curves performed with poly(methyl methacrylate) (PMMA) suggests the values $T_1 \approx T_g + 50°\text{C}$ and $B_0 \approx 15$. In this case, J_{anel} is given by:

$$J_{\text{anel}} = \int_{\ln \tau_\beta}^{\ln \tau_{\max}} A\left\{1 - \exp\left[-\left(\frac{t}{\langle\tau\rangle}\right)\right]\right\} P(\ln \tau)\, \mathrm{d}(\ln \tau) \tag{9}$$

with

$$P(\ln \tau) = \frac{1}{B\sqrt{2\pi}} \exp\left[-\left(\frac{\ln(\tau/\tau_{\max})}{\sqrt{2}B}\right)^2\right]$$

It can be checked that, for low applied stresses σ, both formulations (8) and (9) lead to very similar results.

In addition, the increase of the applied stress σ corresponds to an evolution of the shape of the distribution of characteristic times τ. This evolution is not easy to take into account with the approximation of 'stretched exponential function'. Therefore the single complete formulation (9) with an integration is able to account for the non-linearity of compliance when the applied stress increases.

In all cases, the viscoplastic component of the creep compliance function is generally written as[6]:

$$J_{\text{visc}} = A'(t/\tau_{\max})^{\chi'} \tag{10}$$

In this formulation, χ' is another correlation parameter characterizing the ability of chain reorientation around the SMD when time becomes long enough[8]. In the present investigation, creep tests were conducted at short times; thus this second correlation parameter is neglected. We use $\chi' \approx 1$, though the value 0.6–0.9 is often reported[11] for higher creep times, and A' will have the same value as A (these two values represent the same effect (defect concentration)). Thus, J_{visc} becomes:

$$J_{\text{visc}} = A(t/\tau_{\max}) \tag{11}$$

Finally, the creep compliance function will be given by the following theoretical formulation valuable for low applied stresses ($\sigma < \sigma_c$):

$$J_{\text{tot}}(t) = \frac{1}{E_a} + A\left\{1 - \exp\left[-\left(\frac{t}{\tau_{\max}}\right)^{\chi}\right]\right\} + A\frac{t}{\tau_{\max}} \tag{12}$$

where

$$\tau_\beta = \tau_0 \exp\left(\frac{U_\beta}{kT}\right) \qquad \tau_{\max} = \left(\frac{\tau_\beta}{t_0^{1-x}}\right)^{1/\chi}$$

Over a larger range of stress values, the previous formulation is extended to:

$$J_{\text{tot}}(t) = \frac{1}{E_a} + \int_{\ln \tau_\beta}^{\ln \tau_{\max}} A\left\{1 - \exp\left[-\left(\frac{t}{\tau_{\max}}\right)\right]\right\} \times P(\ln \tau)\, \mathrm{d}(\ln \tau) + A\frac{t}{\tau_{\max}} \tag{13}$$

where

$$P(\ln \tau) = \frac{1}{\sqrt{2\pi}B} \exp\left[-\left(\frac{\ln(\tau/\tau_{\max})}{B\sqrt{2}}\right)^2\right]$$

$$\tau_\beta = \tau_0 \exp\left[\frac{U_\beta}{kT}\left(1 - \frac{\sigma}{\sigma_0}\right)^{3/2}\right] \qquad \tau_{\max} = \left(\frac{\tau_\beta}{t_0^{1-x}}\right)^{1/\chi}$$

In the next part of this article, the experimental data for bulk amorphous PET and bioriented films performed for $\sigma < \sigma_c$ will be decorrelated by using formulation (12). Later, the experimental data will be compared with the predictions given by formulation (13) available for a larger range of stress including the critical value σ_c.

Assuming that the experimental data are fitted by equation (12), the three parameters A, $\tau_{\max}$ and χ are characteristic of the material. These coefficients are adjusted so that the norm $\|J_{A,\tau_{\max},\chi} - J_{\exp}\|$ is minimized. This is equivalent to cancelling the three partial derivatives $\partial/\partial A$, $\partial/\partial \tau_{\max}$ and $\partial/\partial \chi$ of this norm. A Newton–Marquardt numerical method is used.

This resolution poses the following questions:

(i) *Does this approach provide a satisfactory model for the creep behaviour of bulk amorphous PET?* Taking into account both experimental and numerical errors, it is possible to fit each experimental curve $J_{\exp}(t)$ by one theoretical curve $J_{A,\tau_{\max},\chi}(t)$ within an accuracy of 5%. This means that the answer to the question is yes.

(ii) *What is the accuracy of minimized coefficients* A, $\tau_{\max}$ *and* χ? Having identified the two main origins of errors, namely time limit (at most t_f) and number of discretization points (about 50), the following numerical experiment was carried out. Having prescribed one set of initial values A, $\tau_{\max}$ and χ, the corresponding theoretical curve $J_{A,\tau_{\max},\chi}(t)$ is discretized into 30 points and the time limit t_f is chosen lower than $\tau_{\max}/10$. Then, this artificial set of experimental data is refitted by means of the computer code, which provides a new set of coefficients A, $\tau_{\max}$ and χ. It was observed that in each case, the deviation between the two sets of coefficients remains lower than 0.1%, which is quite satisfactory.

(iii) *Is the approximation* $\chi' \approx 1$ *for viscoplastic behaviour justified?* Provided that t_f is lower than $(2–5)\tau_{\max}$, the theoretical curves obtained for $\chi' \approx 1$ or for $\chi' \approx 0.6$ to 0.9 are very close to each other.

Typical values of A, $\tau_{\max}$ and χ obtained with this technique for bulk amorphous PET in the linear domain and for $T \approx 60°\text{C}$ are:

$$A \approx 2 \times 10^{-9}\ \text{Pa}^{-1} \qquad \tau_{\max} \approx 1200\ \text{s} \qquad \chi \approx 0.27$$

These orders of magnitude obtained by analysis of creep tests are in good agreement with the data obtained by analysis of other types of experimental data such as mechanical spectrometry[11].

CASE OF BIAXIALLY ORIENTED THIN PET FILMS

The molecular model of deformation of amorphous PET previously developed cannot be directly used to analyse the experimental data obtained with thin biaxially oriented PET films because of their composite structure (two phases, amorphous and crystalline, which have very different mechanical behaviours).

The behaviour of the first component (amorphous) is supposed to be described by the same theoretical approach as for bulk amorphous PET (i.e. viscoelastic and viscoplastic behaviours), characterized through the three parameters A, $\tau_{\max}$ and χ and an elastic Young's modulus of about the bulk value, 2 GPa in the in-plane direction. Following this assumption, we expect the elastic properties not to be disturbed too much by

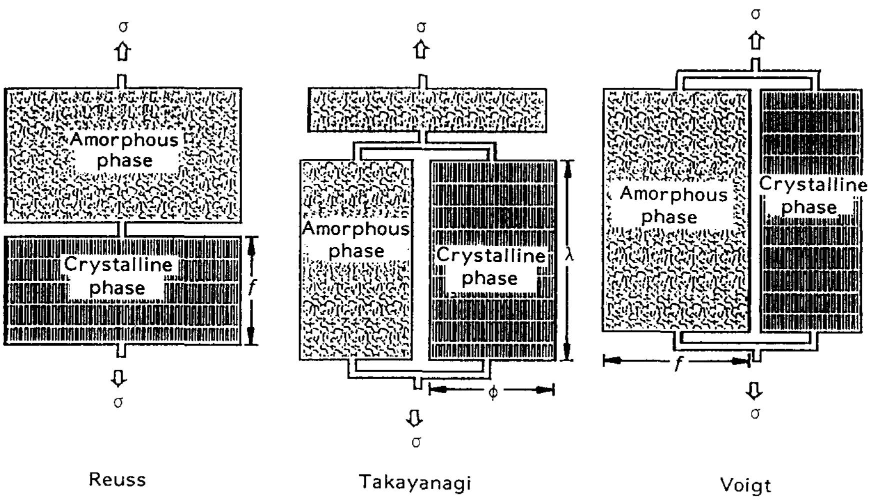

Figure 3 Reuss, Takayanagi and Voigt models

stretching. A, $\tau_{\max}$ and χ of the amorphous phase of both thin semicrystalline films and bulk PET will be compared later in order to verify the validity limits of this hypothesis.

The second component (crystalline) can be considered in our stress domain as a perfect crystal (so, with a creep function defined by $J(t) = 1/E_{c\parallel}$ in the in-plane direction). The assumption that viscoelasticity of the semicrystalline material is entirely due to the contribution of the amorphous phase is satisfactory because of the low magnitude of the strain. Within this framework, the crystalline phase acts just as an inert and stiff part. The elastic Young's modulus value $E_{c\parallel}$ of this ideal PET crystal has been previously estimated by several authors. The values were found in the range 76 to 149 GPa[12–14] and are in very good agreement with that of the structure chain of poly(ethylene terephthalate) crystal lattice, which consists exclusively of the stretched chain conformation[15–17]. Moreover, Treloar[13] estimated this value to be about 124 GPa from theoretical considerations based on atomic displacements and potential-energy distribution. In this paper, the most recent estimation equal to 110 GPa[14] is retained. Note that these high values of Young's modulus are only available in the in-plane direction (because of the mechanical stretching). In the thickness direction, the elastic modulus $E_{c\perp}$ of the lamellar region is probably about 6 GPa. This very low value (same order as for amorphous PET) can be easily explained by the strong anisotropy of these thin films: the crystallinity is only induced by orientation in the plane direction and there is no alignment of chains in the thickness direction.

Let us now introduce a coupling law of both mechanical responses (amorphous and crystalline) in order to explain the mechanical behaviour of the partially crystalline films during creep tests conducted in the in-plane direction. Then the partial behaviour law of the amorphous phase is extracted from the global behaviour law in order to compare it with the mechanical behaviour of totally amorphous PET.

Without specific information about the coupling law of both phases within the bounds defined by Voigt's model and Reuss's model, a simple and phenomenological model previously proposed by Takayanagi[18] will be used. This model is based on a mixing law between the Voigt lower bound and the Reuss upper bound of the creep compliance function of a two-phase system as shown in *Figure 3*. These bounds correspond with a parallel (Voigt) and a series (Reuss) mixing rule of the two phases (amorphous and crystalline) in relation to the creep direction[18,19]. Thus, this model is built by connecting in series the amorphous element A with the parallel model of crystalline (C) and amorphous (A) elements. This connection A–(C//A) is physically more meaningful than C–(C//A) because of the dispersion of crystalline units in a continuous amorphous phase.

The two Reuss and Voigt bounds and Takayanagi's mixing law are given by:

$$J_R = (1 - f)J_a + fJ_c \qquad \text{Reuss} \qquad (14a)$$

$$\frac{1}{J_T} = \frac{1 - \varphi}{J_a} + \frac{\varphi}{\lambda J_c + (1 - \lambda)J_a} \qquad \text{Takayanagi} \qquad (14b)$$

$$\frac{1}{J_V} = \frac{1 - f}{J_a} - \frac{f}{J_c} \qquad \text{Voigt} \qquad (14c)$$

The Takayanagi formulation introduces two internal parameters, λ and φ, linked by the relation $\lambda\varphi = f$ where $f \approx 0.42$ is the volume fraction of the crystalline phase. The values of parameter λ range between f (Reuss's limit) and 1 (Voigt's limit). In a first step, λ is calculated by introducing the stress–strain relations for an applied stress in the in-plane direction, $\sigma = E\varepsilon$, with the different moduli E_{sc}, E_c and E_a instead of $1/J_T$, $1/J_c$ and $1/J_a$ respectively in the Takayanagi equation (14b). The value of λ results from:

$$\lambda(E_{sc} - E_a)(E_c - E_a) = E_c(E_{sc} - E_a) - fE_a(E_c - E_a) \qquad (15)$$

If E_c is much greater than E_a and E_{sc}, this relation becomes:

$$\lambda \approx 1 - \frac{fE_a}{E_{sc} - E_a} \qquad (16)$$

With the previous numerical values ($E_a \approx 2$ GPa and $E_{sc} \approx 4.7$ GPa) and formulation (16), we find $\lambda \approx 0.69$ and $\varphi \approx 0.61$.

The influence of the extraction technique on the values of λ and φ is studied. For that purpose, the effect of the approximations $E_c \gg E_a$ and $E_c \gg E_{sc}$ can be evaluated by computing λ in the two extreme cases, by using equation (15):

for $E_c = 76$ GPa (minimum literature value) $\lambda \approx 0.70$

for $E_c = 149$ GPa (maximum literature value) $\lambda \approx 0.71$

In addition, the order of magnitude of λ, intermediate between 0.42 (Reuss limit) and 1 (Voigt limit), means that the system structure is neither purely series nor purely parallel.

In a second step, in order to obtain $J_a(t)$ as a function of $J_{sc}(t)$, E_c, λ and f, the three creep compliance relations $J = \varepsilon/\sigma$ for the three materials (respectively bulk amorphous, semicrystalline and totally crystalline) are used in equation (14b). We suggest extending relation (14b) previously introduced for elastic behaviour (value of Young's modulus) to the non-elastic compliance. One obtains:

$$(1-\lambda)E_cJ_a(t)^2 + [\lambda - (1-\lambda+f)E_cJ_{sc}(t)]J_a(t) - (\lambda - f)J_{sc}(t) = 0 \qquad (17)$$

From equation (16), we obtain too:

$$\frac{E_{sc}}{E_a} = \frac{1+f-\lambda}{1-\lambda} \qquad (18)$$

If E_c is much greater than E_a and E_{sc}, relation (17) can be simplified:

$$J_a(t) = \frac{E_{sc}}{E_a} J_{sc}(t) \qquad (19)$$

With this new formulation, it will be possible to calculate the creep compliance function of the amorphous phase included in semicrystalline films by using equations (12) and (19) in order to compare theoretical and experimental data. Therefore, the three parameters A_{am}, $\tau_{max,am}$ and χ_{am} of the amorphous phase are deduced from the semicrystalline parameters:

$$A_{am} = \frac{E_{sc}}{E_a} A_{sc} \qquad \tau_{max,am} = \tau_{max,sc} \qquad \chi_{am} = \chi_{sc} \qquad (20)$$

The final values of parameters A, τ_{max} and χ depend on the resolution, on the approximations and on the assumed values of various parameters (E_c, f, ...). It is worth evaluating the influence of these effects.

Owing to the assumptions $E_c \gg E_a$ and $E_c \gg E_{sc}$, equation (17) has been simplified (cancelling of the last term) and solved, yielding equation (19). This approximate solution (independent of E_c and f) is compared with the exact one (using equation (17)), for the following set of parameters:

$$76 \text{ GPa} < E_c < 149 \text{ GPa}$$
$$0.35 < f < 0.49$$
$$0 < J_{sc} < 5/E_{sc}$$
$$E_a = 2 \text{ GPa} \qquad E_{sc} = 4.7 \text{ GPa}$$

The relative deviation between the 'exact' solution and the 'approximate' one is a decreasing function of E_c (equal to zero when $E_c \to \infty$), an increasing function of J_{sc} and a decreasing function of f. However, the maximum value of this deviation (obtained for $E_c = 77$ GPa, $f = 0.35$ and $J_{sc} = 5/E_{sc}$) is lower than 5% (same order of magnitude as the accuracy of experimental errors). We conclude that even though the accuracy of basic parameters E_c, f and J_{sc} is low, it does not affect the validity of this approach.

Figure 4 represents the two 'extracted' creep compliance curves (amorphous and crystalline) together with the semicrystalline curve and the bulk amorphous one (at a lower temperature $T = 62°C$). The three extracted values of A, τ_{max} and χ associated with the amorphous phase behaviour in the linear domain are displayed in *Table 2* for three temperatures. The following comments can be made:

(i) A is significantly lower for the extracted amorphous phase than for bulk amorphous (570×10^{-12} Pa^{-1} against 2000×10^{-12} Pa^{-1}).

(ii) In both cases, A is not very sensitive to temperature.

(iii) τ_{max} is much larger for the extracted amorphous phase than for bulk amorphous (3 h against 20 min).

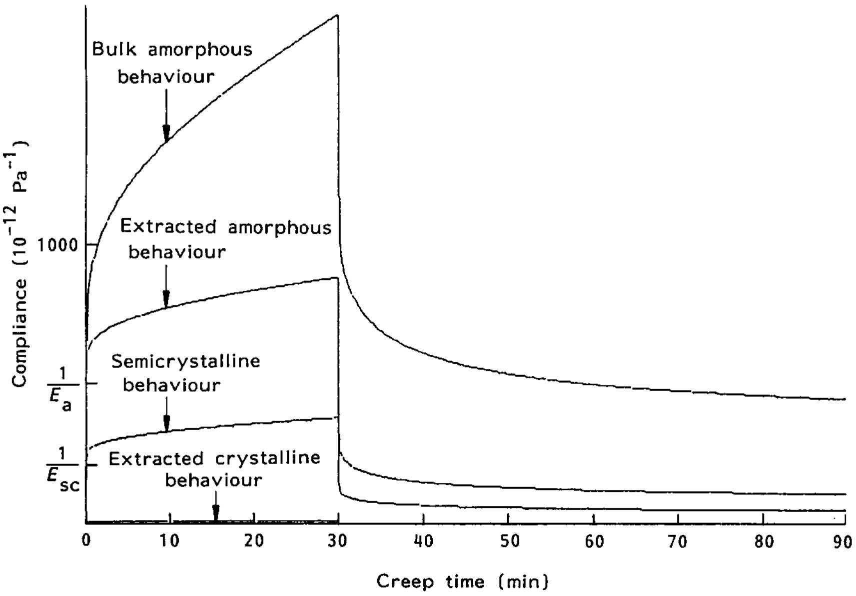

Figure 4 Experimental creep curves of bulk amorphous PET (60°C), semicrystalline film (77°C), extracted amorphous phase (77°C) and extracted crystalline phase (77°C)

Table 2 Dependence of the three parameters A, τ and χ on temperature for biaxially oriented films and their extracted amorphous part in linear domain

	Semicrystalline			Extracted amorphous part		
Temperature (°C)	A (10^{-12} Pa^{-1})	τ (h)	χ	A (10^{-12} Pa^{-1})	τ (h)	χ
46	250	4.2	0.22	570	4.2	0.22
59	250	3.1	0.23	570	3.1	0.23
77	220	2.2	0.25	530	2.2	0.25

(iv) In both cases, τ_{max} is a strongly decreasing function of temperature.

(v) χ is slightly lower for extracted amorphous phase than for bulk amorphous (0.23 against 0.27).

Now, a physical interpretation of these results is proposed.

(i) According to the physical meaning of parameter A, this result indicates that the defect concentration in bulk amorphous material is larger than in biaxially oriented films. This is consistent with direct approaches of polymer conformations.

For instance, Heffelfinger and Schmidt[16] studied by infra-red techniques the chain conformation of PET films submitted to mechanical stretching. They distinguished two different conformations: first a '*trans* structure' corresponding to an extended form and secondly a '*gauche* structure' corresponding to a relaxed and unextended form. For isotropic PET, they observed 13% of randomly oriented *trans* conformations and 87% of *gauche* conformations.

Mechanical stretching leads to extension and alignment of the individual chains in the direction of stretching and thus induces an increase of *trans* state ratio. When several chains in the *trans* conformation are close enough to each other, crystallization occurs. However, Heffelfinger and Schmidt observed that, although crystallization tends to reduce the proportion of chains in the *trans* state, the ratio of *trans* state globally increases during stretching (13 to 31% for a stretching ratio of 4).

The concept of 'defect', as introduced in the theoretical model developed here, corresponds to a microdensity, enthalpy or entropy fluctuation by comparison with the equilibrium position. From this point of view, the pure crystal corresponds to the perfect state (no defect) and conversely the *gauche* conformation can be regarded as forming a defect. Thus, a larger amount of *gauche* units is in good agreement with an increase of parameter A, which is proportional to defect concentration.

(ii) If no structural transformation occurs, defect concentration remains constant for $T < T_g$, which is consistent with a weak dependence of parameter A *versus* temperature.

(iii) In biaxially oriented PET films, crystalline lamellae reduces the segmental mobility of chains of the amorphous phase, corresponding to an increase of characteristic time τ_{max}. The same reason explains the shift towards higher value of T_α, the temperature of the main (or α) mechanical relaxation in the case of semicrystalline films (about 90°C against 75°C for bulk amorphous PET).

A few years ago, Struik[20] attempted an explanation based on perturbation due to the crystal lattice. This approach is similar to a well known model for filled rubbers, in which carbon black particles restrict the mobility of parts of the rubbery phase. Thus, Struik suggests the existence of two different amorphous regions in semicrystalline polymers: first a region of reduced mobility due to vicinity of crystals and secondly an undisturbed region where properties become equal to those of the bulk amorphous material.

The crystalline phase of thin biaxially oriented PET films induced by mechanical stretching has been studied[11] by X-ray diffraction and small-angle X-ray scattering. Crystallite length was found to be 4 nm with broadening of ($1\ 0\ \bar{5}$) diffraction peak and long period (sum of crystallite thickness and intercrystalline thickness and intercrystallite spacing) of about 10 nm using the Bragg equation. Thus, amorphous length can be calculated by subtracting the average crystallite length from long-period spacing: we found a value of about 6 nm. Similar results were found by d.s.c. measurements[21]. Comparing these values (4 nm crystal and 6 nm amorphous) with the period of molecular chain length (1 nm), it is seen that each segment of amorphous PET is likely disturbed by a neighbouring crystalline element.

Therefore, Struik's second region (where amorphous phase has the same mobility as bulk amorphous PET) probably does not exist in thin biaxially oriented films. It implies that the values of τ_{max} only concern the disturbed region (no contribution of the undisturbed one).

Moreover, various authors[11,22] have shown that, even for long ageing time (and thus, for any nominal value of relaxation time), biaxially oriented films have no significant ageing. The gap between the two ageing behaviours does not follow a simple mixing law between the two phases of semicrystalline films. This experimental result indicates that, apart from the increase of characteristic relaxation time due to crystal lattice disturbance, defect impoverishment in the amorphous phase around crystalline lamellae is probably the main factor that can explain why the effects of physical ageing in thin biaxially oriented PET are negligible in accordance with the molecular interpretation of structural relaxation in terms of defect annihilation[8].

(iv) τ_{max} is an increasing function of characteristic time τ_β (equation (7)), whereas τ_β is a strongly decreasing function of temperature (following Arrhenius equation (2)).

(v) According to the theoretical model, a low value of correlation parameter χ corresponds to large correlation effects, which also results in a lower molecular mobility (equation (17)).

To sum up, all the experimental observations are in full agreement with the physical interpretation of the parameters defined in the model. The main result is that mechanical stretching of a thin PET film induces structural changes in its amorphous region. These

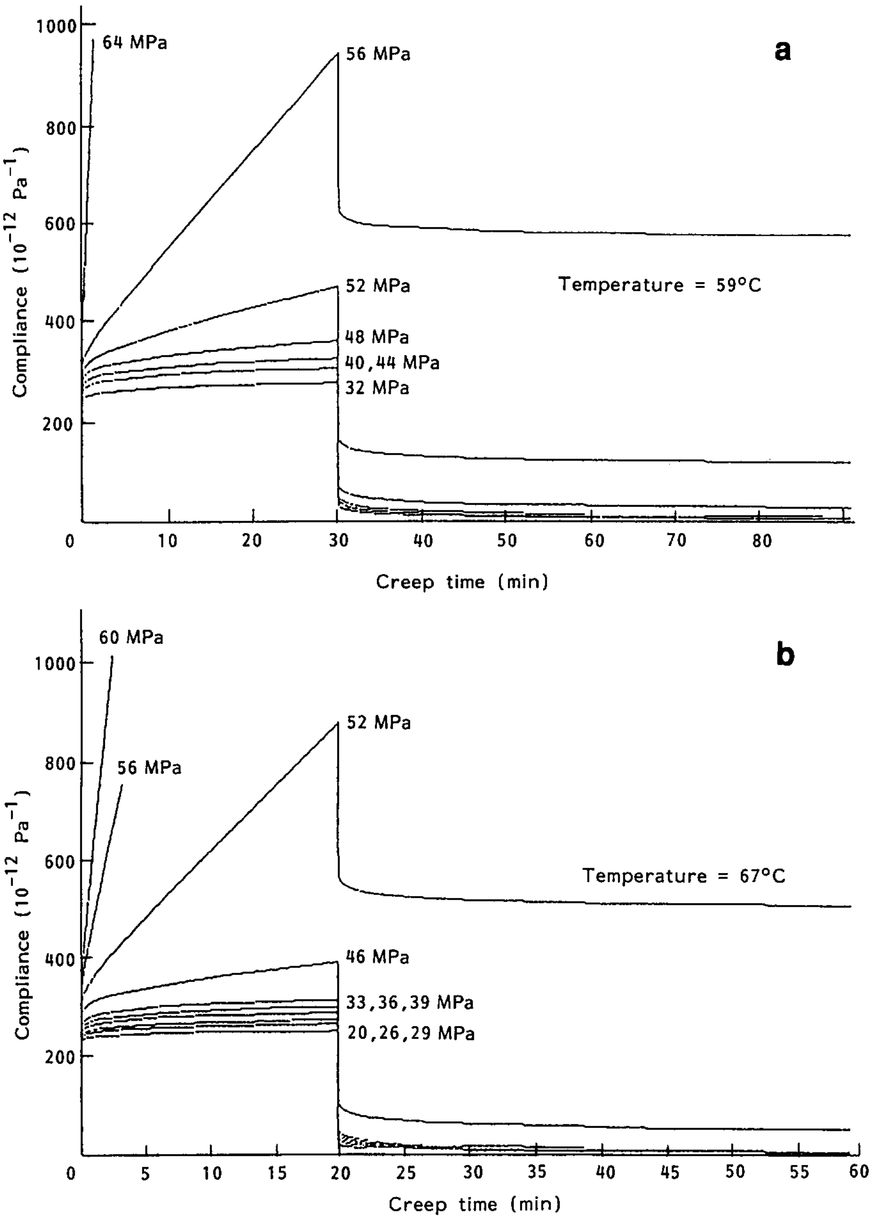

Figure 5 Theoretical curves calculated for the same conditions (stress and temperature) as for results of *Figure 1a* and *Figure 1b* respectively

changes can be regarded as a lower concentration of defects, implying also a reduced molecular mobility. Following this point of view the dynamic modulus of the amorphous phase is likely a little higher than for bulk amorphous phase (2 GPa).

COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL CURVES FOR BIAXIALLY ORIENTED PET FILMS UNDER MEDIUM STRESSES

When the applied stress exceeds the domain of 'small stresses', the compliance function is no longer represented by equation (12), resulting from a simplified distribution of characteristic times, but more fruitfully by equation (13), involving (i) a Gaussian distribution of characteristic times and (ii) a stress dependence of τ_β, the latter feature being obviously the most important.

In order to attempt an interpretation of the experimental data obtained for 'medium stresses' (*Figures 1a* and *1b*), theoretical creep curves are plotted by using equations (13) for amorphous phase and (19) for the mechanical coupling effect, for the same conditions (stress and temperature) and with the following set of parameters:

$E = 4.7$ GPa $\qquad A = 250 \times 10^{-12}\ \text{Pa}^{-1}$

$\sigma_0 = 0.3$ GPa $\qquad U_\beta = 60\ \text{kJ mol}^{-1}$

$t_0 = 10^{-5}$ s $\qquad B(T) = 15(1 + 400\ \text{K}/T)$

$\tau_0 = 10^{-13}$ s

E and A come from the present study (direct measurement for E and use of simplified equation (12) for A). σ_0, U_β and τ_0 can be found in the literature dealing with polymer physics. t_0 and B are chosen from experimental data[6,10]. These curves have been reported on *Figure 5a* ($T = 59°\text{C}$) and *Figure 5b* ($T = 67°\text{C}$).

This approach is too rough to lead to quantitative agreement, but the main experimental features can be explained: (i) The theoretical and experimental curves exhibit the same general shape, even at small stress level, as quoted before. Their deviation still increases as the applied stress increases. After recovery, the curves become nearly superimposed. (ii) The theoretical model enables the sudden change in the creep curves to be predicted. When the applied stress becomes higher than some critical value, say σ_c, compliance rapidly increases with stress, as observed experimentally. (iii) The critical value of the stress (σ_c) is a decreasing function of temperature (both theoretical prediction and experimental result).

These first results show that a straightforward extension of a theoretical model essentially based on the concept of 'hierarchically correlated molecular movements' and 'defects' predicts the same tendencies as does experiment. In order to improve this approach, it would be necessary to have—among others—a better knowledge of the general behaviour of defects under stress.

CONCLUSIONS

The aim of this work was: (i) to validate the extension of the theoretical model previously proposed in the case of non-linear behaviour of amorphous polymer, submitted to non-elastic deformation; (ii) to separate the mechanical responses of both amorphous phase and crystallites of biaxially oriented PET films and to compare the former to that of bulk amorphous PET; and (iii) to predict the mechanical behaviour of biaxially oriented PET films under medium stresses.

Creep tests were carried out with thin biaxially oriented films and with bulk amorphous PET. A theoretical model of deformation already developed for glassy solids has been recalled and extended to take into account the existence of a non-linear component above some critical stress σ_c. For that purpose, a global approach generalizing the formulation available for low stresses has been proposed. Each parameter introduced in the theory possesses a clear physical meaning and the main experimental features are explained, e.g. the decrease of the critical stress σ_c with increasing temperature is predicted.

In the present study, biaxially oriented PET films are considered as two-phase systems composed of amorphous and crystalline regions, following Takayanagi's mixing law. This approach allows us to understand the geometrical distribution of the two phases and results in pertinent information about each phase. For instance, the amorphous phase of biaxially oriented PET films is shown to exhibit a lower concentration of defects (due to conformation change) and to be strongly disturbed by crystalline lamellae.

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