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β- and α-relaxations in poly(methyl methacrylate) and polycarbonate: non-linear anelasticity studies by antistress relaxation

R. Quinson* and J. Perez*
Laboratoire GEMPPM, UA CNRS 341, INSA Lyon, 69621 Villeurbanne, France

and Y. Germain and J. M. Murraciole
Centre d'étude de recherche et développement, Elf Atochem, 27470 Serquigny, France
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A new test, known as antistress relaxation, allows us to study, exclusively, the anelastic deformation, i.e. one which is recoverable with time, of various polymers over a wide range of stresses and temperatures until the yield flow point is reached. In the linear regime, this test is linked with certain viscoelastic properties, such as the loss tangent, tan ϕ and the loss dynamic compliance, J'', which are usually measured using dynamic spectrometry techniques. Thus, the isochronal J'' and tan ϕ spectra of poly(methyl methacrylate) (PMMA) and polycarbonate (PC) are obtained by performing this test at several different temperatures. These spectra are very similar to those obtained using classical techniques and clearly display the β-relaxation and the anelastic part of the α-relaxation. When carried out at high stress levels, the antistress relaxation test allows us to obtain these spectra in the non-linear regime, and therefore, carry out observations of the two relaxations under high stresses. In particular, it is noticeable that the stress increase leads to an important shift of the anelastic part of the α-relaxation towards low temperatures and, eventually, to merging of the α- and β-relaxations. On the other hand, there is no clear evidence for any effect of the stress on the β-relaxation, which, in any case, appears to remain weak. Taking into account these observations, different models, describing the non-linear anelastic deformation during creep experiments, are discussed. Finally, from the hypothesis and the concepts developed in the molecular model of Perez, an energy scheme is proposed for representing the energy state of the microregions of the material participating in anelastic and plastic deformation. This energy representation is able to describe the experimental results concerning the α- and β-relaxations under high stress, and also various other previous experimental observations.

(Keywords: polycarbonate; poly(methyl methacrylate); anelasticity)

INTRODUCTION

The non-elastic deformation of amorphous polymers in the solid state has been studied by many researchers for several decades. In addition to the great interest that the physics of amorphous solids has aroused, the technological consequences of such a phenomenon are unquestionable.

This non-elastic deformation includes both anelastic deformation, which is fully recoverable on unloading, and plastic deformation, which is an irreversible process unless the temperature rises above the glass transition temperature, T_g. These two types of deformation have been studied and modelled, on the one hand, with descriptions of the anelastic deformation generally using phenomenological models of viscoelasticity, and on the other hand, with theories concerning the yield behaviour. Among these theories, very few have tried to establish a link between these two types of deformation, although nobody can assert that these two types of strain are independent or, from a molecular point of view, that the processes leading to each of these two types of deformation are fundamentally different. Therefore, in the last part of this paper, we will try to give a physical explanation of the anelastic strain and also the probable connection existing between these reversible and irreversible processes.

To study experimentally the anelastic strain, the use of classical mechanical tests (tensile, compressive, creep, etc.) is not well suited. Indeed, these tests do not allow a very precise determination of each component of the inelastic deformation. Even the stress relaxation test can reflect the evolution of the two different types of inelastic strain. Indeed, at strains below plastic flow conditions, the decrease of the stress during this test mainly reflects the increase of anelastic strain whereas, above the yield point, it reflects mainly the increase of the plastic strain. We have therefore developed a new type of test, which we shall call the 'antistress relaxation' test, which allows the exclusive observation of the anelastic strain, and of

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* To whom correspondence should be addressed

its non-linear behaviour until the yield stress point is reached.

EXPERIMENTAL

We have studied two amorphous polymers, namely PMMA ($T_g = 123°C$, $M_n = 3\,000\,000$) and PC ($T_g = 152°C$, $M_n = 23\,330$), which were provided by Elf Atochem. Both polymers were cooled from a temperature $T > T_g$, and then annealed for 1 day at a temperature of $T_g - 30°C$ in order to minimize any ageing effects during the measurements.

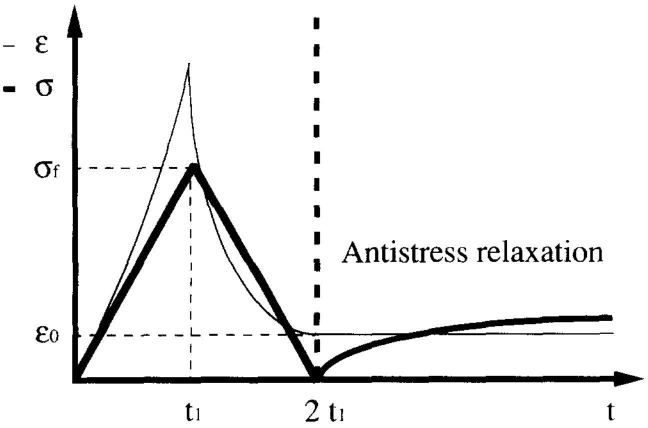

Figure 1 The antistress relaxation test principle

For mechanical testing, we used cylindrical samples with a diameter of 8 mm and a length of 12 mm. The tests have been performed in the uniaxial compression mode using an Adamel Lhomargy DY25 machine with a 20 kN cell, which was equipped with a cooling chamber, thus allowing measurements to be made over the range from −150 to 150°C under a controlled atmosphere of nitrogen gas. For experimental convenience, all samples were preloaded using a force of 500 N (~10 MPa) before being tested.

The antistress relaxation test consists of three stages (*Figure 1*). First, a constant load rate is applied during a time t_1 until a maximum stress σ_f is reached. Secondly, the sample is unloaded at the same rate during a further time t_1. Finally, the strain ε_0 is maintained constant, which then leads to an antistress relaxation. Indeed, the anelastic strain produced during the first two stages is not totally recovered at $t = 2t_1$, and consequently the resulting intrinsic recovery will create this antistress relaxation. A simple rheological scheme (*Figure 2*) illustrates the origin of this stress. Other authors[1] have also observed such an antistress relaxation, and have described it by using a two-process model which is similar to the one illustrated in *Figure 2*.

Although this type of test is very difficult to perform under conditions leading to large plastic flow, it can be realized if only a small amount of plastic strain occurs during the first two steps and, in any case, this antistress

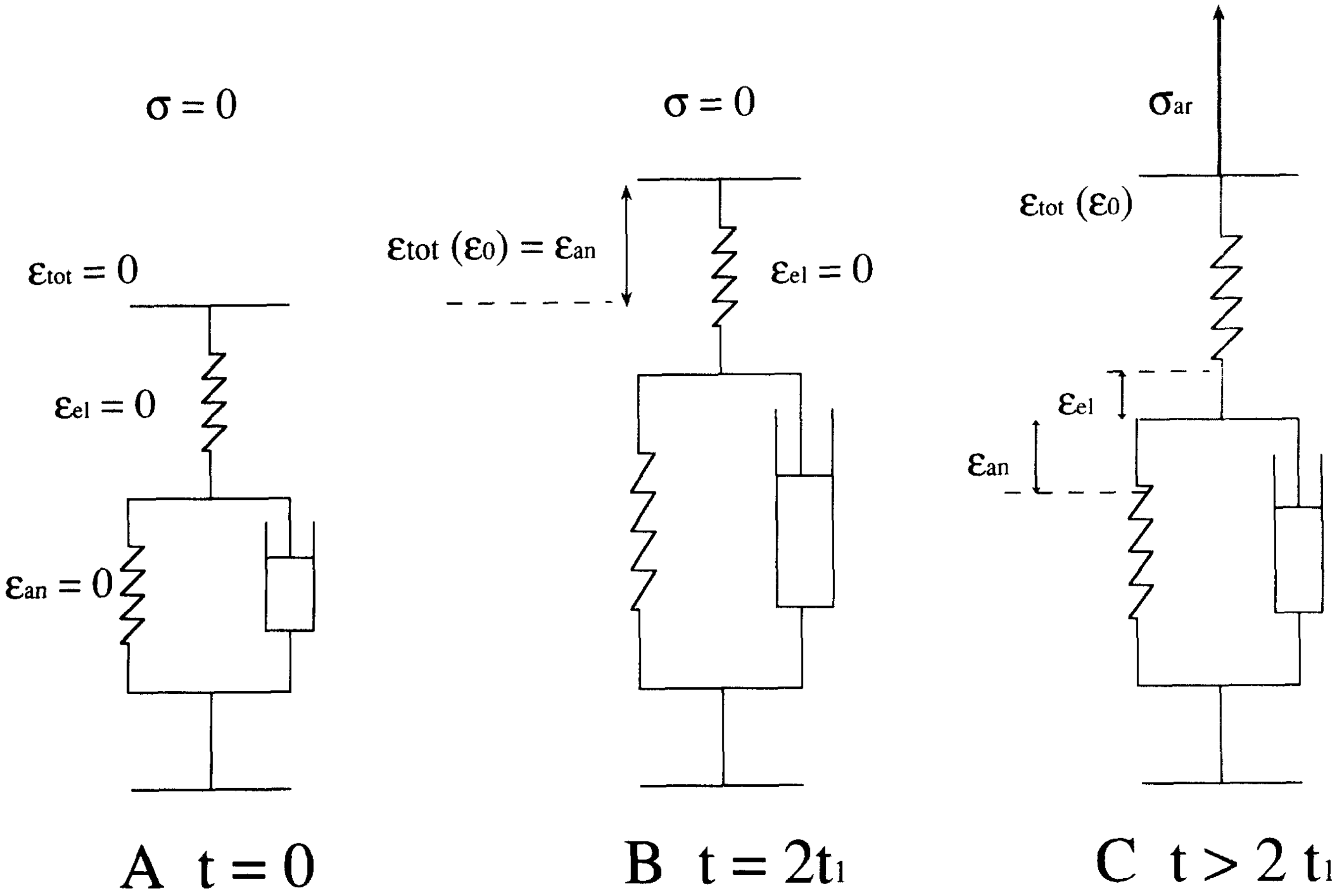

Figure 2 Rheological scheme describing the behaviour of the material during the antistress relaxation test. The spring and the 'Voigt' element represent, respectively, the elastic and the anelastic behaviour; the corresponding deformations are ε_{el} and ε_{an}. (a) At the beginning: $\sigma = 0$, $\varepsilon_{el} = 0$, and $\varepsilon_{an} = 0$. (b) After loading and unloading: $\sigma = 0$, $\varepsilon_{el} = 0$, and $\varepsilon_{an} = \varepsilon_0 \neq 0$. (c) At constant deformation (ε_0), the relaxation of the material, corresponding to a reduction of the anelastic deformation, leads to an elastic deformation and then to an antistress σ_{ar}

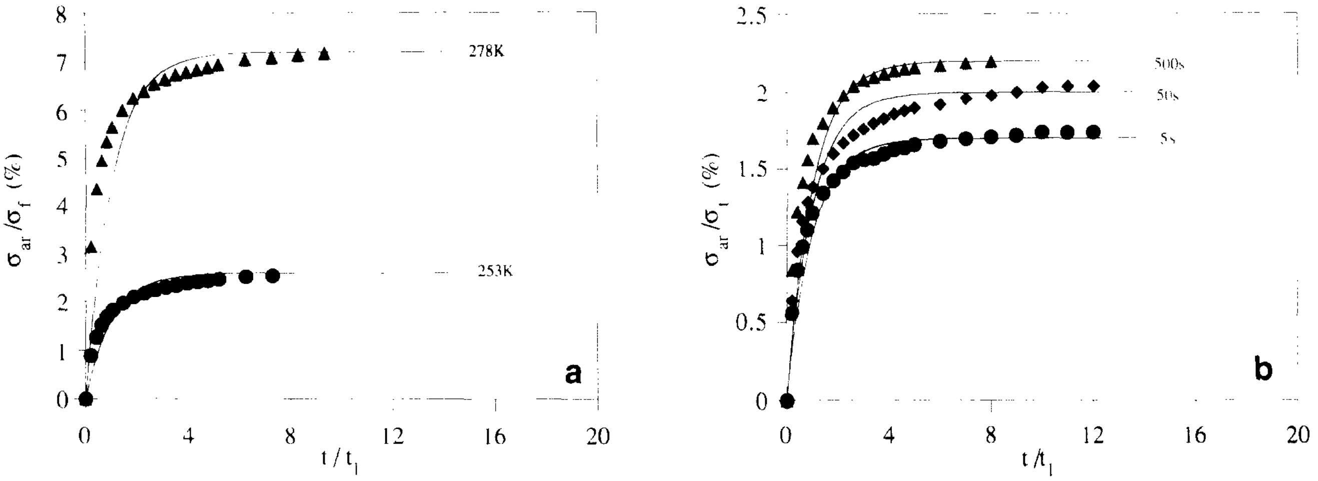

Figure 3 The antistress signal fitted to the following expression in the case of PMMA: $\sigma_{ar}=\sigma_\infty[1-\exp(-t/t_1)]$. (a) Results obtained at different temperatures T with $t_1=12$ s and $\sigma_f=170$ MPa: (▲) 278 K, fitted with $\sigma_\infty=7.2\times10^{-2}\sigma_f$; (●) 253 K, fitted with $\sigma_\infty=2.6\times10^{-2}\sigma_f$. (b) Results obtained at different times t_1 with $\sigma_f=30$ MPa and $T=297$ K: (▲) 500 s, fitted with $\sigma_\infty=2.2\times10^{-2}\sigma_f$; (◆) 50 s, fitted with $\sigma_\infty=2\times10^{-2}\sigma_f$; (●) 5 s, fitted with $\sigma_\infty=1.7\times10^{-2}\sigma_f$

relaxation is only a reflection of the anelastic strain which is not yet recovered at $t=2t_1$.

In this work, several tests have been performed under different conditions in order to observe the effect of the time t_1, the temperature T and the maximum stress σ_f on the antistress σ_{ar}.

RESULTS

From the results shown in *Figure 3*, we can observe that whatever the value of time t_1 ($5\ \mathrm{s}<t_1<500\ \mathrm{s}$), or whatever the values of the two other parameters (T, σ_f), the antistress signal can be approximately fitted to an expression such as the following:

$$\sigma_{ar}=\sigma_\infty\left[1-\exp\left(-\frac{t}{\tau}\right)\right] \quad \text{with } \tau\sim t_1 \qquad (1)$$

However, σ_∞ (σ_{ar} for $t\rightarrow\infty$) depends on each of the three parameters t_1, σ_f and T. Indeed, in *Figure 4*, we can observe this influence of T and σ_f on the antistress. Therefore, we can point out that there is no simple temperature effect, whereas the ratio of σ_{ar}/σ_f shows a non-linear behaviour of the antistress with the maximum applied stress σ_f.

As it is rather difficult to determine the exact value of σ_∞, a more convenient way to study the influence of the temperature and maximum stress is to take the value of σ_{ar} at a given time (proportional to t_1). It is then possible to observe the effect of these two parameters by the same representation. In *Figure 5*, we can observe that for both materials the antistress relaxation is quite small at low temperatures, displaying a shoulder in the case of PMMA, and a peak for PC, whereas at high temperatures it increases dramatically. We can also point out that σ_f has the greatest effect on the last points of each curve (i.e. at the highest temperatures) which seem to be shifted towards lower temperatures as σ_f increases.

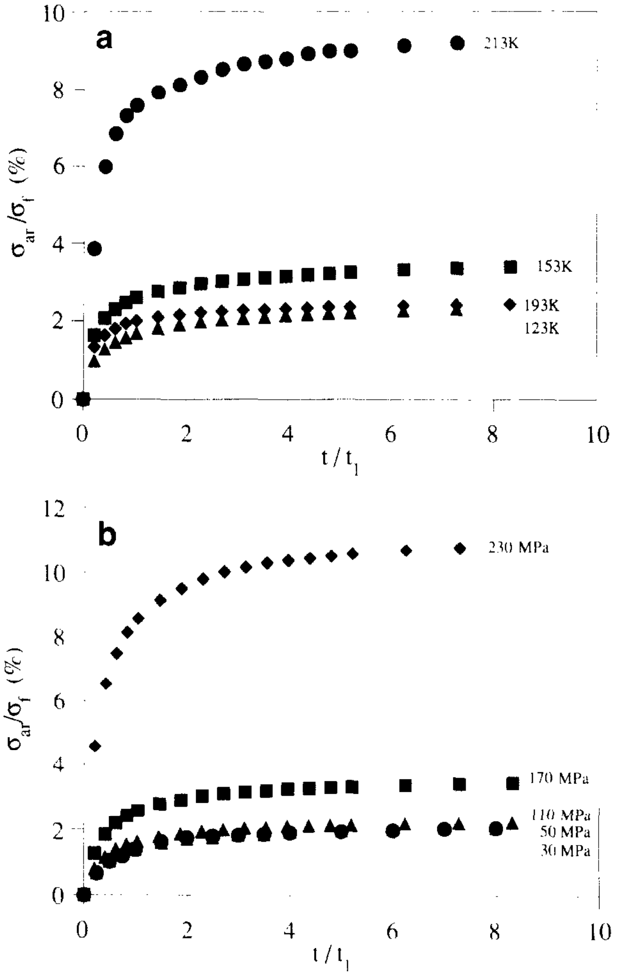

Figure 4 (a) Effect of temperature on the antistress signal for PC, with $t_1=12$ s and $\sigma_f=130$ MPa. (b) Effect of σ_f on the antistress signal for PMMA, with $t_1=12$ s and $T=253$ K

Analysis using the equations of viscoelasticity

It is well established that the equations of viscoelasticity[2,3] are quite suitable for describing the behaviour of polymers in the linear regime. Thus, we can try to analyse this antistress relaxation phenomenon using these equations and, in particular, attempt to establish a link between the signal of antistress relaxation and the different properties of the material.

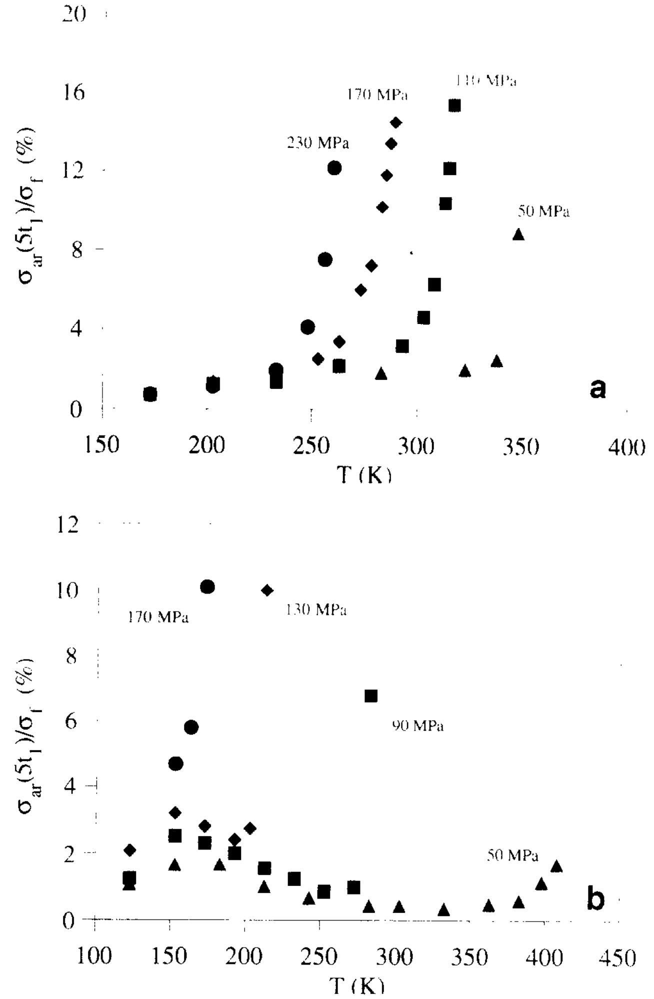

Figure 5 The ratio $\sigma_{ar}(5t_1, \sigma_f)$ vs. temperature for different values of σ_f, with $t_1 = 12$ s: (a) PMMA; (b) PC

First, considering the rheological models shown in *Figure 2*, we obtain the following expression:

$$\sigma_{ar}(t) = E(t)(\varepsilon_0 - \varepsilon_f(t)) \tag{2}$$

where $t = 0$ is taken as the beginning of the antistress relaxation, ε_0 is the constant strain during the last part of the test, $\varepsilon_f(t)$ is a strain corresponding to the one remaining at t if, instead of maintaining the strain constant at $t = 0$, we let it recover by imposing a zero stress rate, and $E(t)$ is the Young's modulus measured at time t. Experimentally, the deformation which is maintained constant during the antistress relaxation corresponds to the deformation of both sample and machine, where the latter behaves as a perfect spring. Consequently, this modulus must be associated with both of these, i.e. $E_{ms}(t)$.

The expressions for ε_0 and ε_f are obtained by the use of the Boltzmann superposition principle, as follows:

$$\varepsilon_0 = \sigma_f\left\{\frac{t_1}{\eta_0} + \int_{-\infty}^{+\infty} L(\tau)\int_0^1\left[1 - \exp\left(-\frac{t_1}{\tau}\right)\right] \times \exp\left[-\frac{t_1(1-n)}{\tau}\right] \mathrm{d}n\,\mathrm{d}\ln\tau\right\} \tag{3}$$

and

$$\varepsilon_f(t) = \sigma_f\left\{\frac{t_1+t}{\eta_0} + \int_{-\infty}^{+\infty} L(\tau)\int_0^1 \exp\left(-\frac{t}{\tau}\right) \times \left[1 - \exp\left(-\frac{t_1}{\tau}\right)\right]\exp\left[-\frac{t_1(1-n)}{\tau}\right]\mathrm{d}n\,\mathrm{d}\ln\tau\right\} \tag{4}$$

The terms t_1/η_0 and $(t_1 + t)/\eta_0$, where η_0 is the steady-flow viscosity, are negligible in all of the cases studied.

In the above equations, $L(\tau)$ is the retardation time function. Below T_g, where the viscosity is very high, this function can, as a first approximation[2], be directly linked to the loss compliance $J''(\tau)$, with $L(\tau) = J''(\tau)2/\pi$, and where $\tau = 1/2\pi N$, with N being the solicitation frequency.

Finally, we obtain for $t = xt_1$ (measurement time proportional to t_1) the following:

$$\varepsilon_0 - \varepsilon_f(t) = \sigma_f \int_{-\infty}^{+\infty} J''(\tau)\frac{2}{\pi}F(x, \tau, t_1)\,\mathrm{d}\ln\tau \tag{5}$$

in which

$$F(x, \tau, t_1) = \left[1 - \exp\left(-\frac{t_1}{\tau}\right)\right]^2\left[1 - \exp\left(-\frac{xt_1}{\tau}\right)\right]\frac{\tau}{t_1} \tag{6}$$

The shape of the function F for $x = 5$ (time $t = 5t_1$) is shown in *Figure 6a*. Compared to the width of the J''

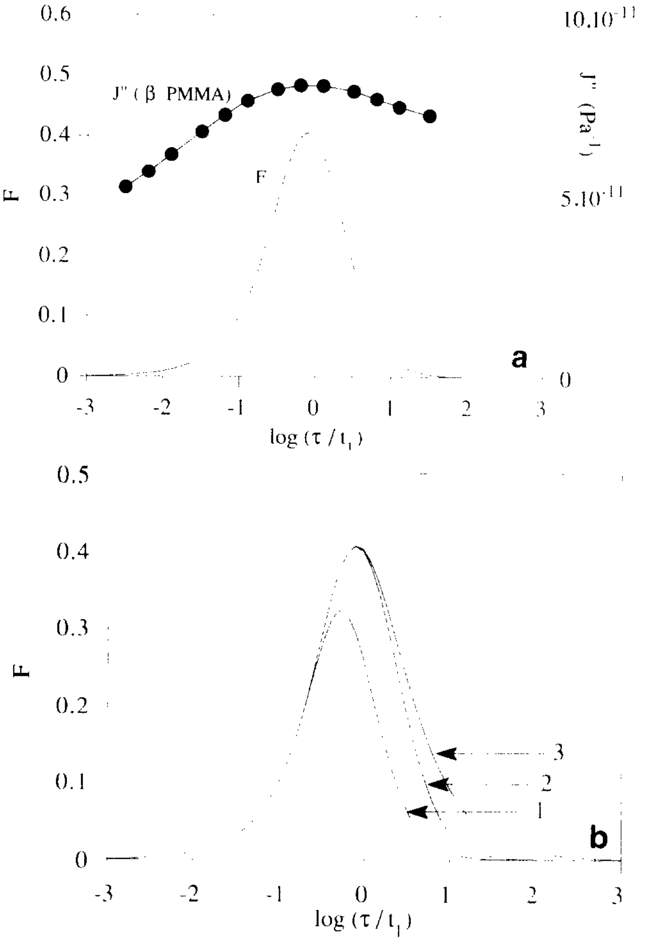

Figure 6 (a) Representation of the filter function F, with $\log(\tau/t_1)$ as the abscissa, showing a comparison of the broadness of the peak corresponding to the function F, and the β-relaxation peak of the isothermal J'' spectrum of PMMA[4] for $T = 256$ K ($t_1 = 1000$ s). (b) Influence of the measurement time on the function F: (1) $x = 1$, measurement time $= t_1$; (2) $x = 5$, measurement time $= 5t_1$; (3) $x = 10\,000$, measurement time $= 10\,000t_1$

β-relaxation peak observed for PMMA[4], this function is clearly narrower. Therefore, we can consider that F acts as a filter function. The last expression can then be approximated (as it is not a perfect filter) as follows:

$$\varepsilon_0 - \varepsilon_f(t) = \sigma_f J''(\tau_{moy})\left(\frac{2}{\pi}\right)A_f \tag{7}$$

in which

$$A_f = \int_{-\infty}^{+\infty}\left[1-\exp\left(-\frac{t_1}{\tau}\right)\right]^2\left[1-\exp\left(-\frac{xt_1}{\tau}\right)\right]\frac{\tau}{t_1}\,\mathrm{d}\ln\tau \tag{8}$$

$J''(\tau_{moy})$ is the average filtered value of J'', and is approximately the same as the J'' value corresponding to the characteristic time at the maximum of the F function, since it appears similar to a Gaussian function.

For $x = 5$, we can determine that $A_f = 1.22$ and $\tau_{moy} \sim t_1$. This explains the good fit of the antistress relaxation signal with only one characteristic time, i.e. $\tau = t_1$.

It is worthwhile here to describe the actual effect of x on the function F. In fact, an increase in x leads to an increase in A_f, but also to a broader peak (*Figure 6b*). Therefore, the measured signal is more important, thus permitting a smaller relative error in the σ_{ar} values but in this case the function F acts less effectively as a filter. Conversely, a smaller value of x leads to a better filter, but also to a greater relative error in the measurement. From an experimental point of view, $x = 5$ seems to be a good compromise.

Moreover, we must realize that by changing either t_1 or the temperature T (corresponding in both cases to a shift of J'' as represented in *Figure 6a*), allows us to obtain J'' values corresponding either to different characteristic times at a given temperature, or to different temperatures at a given time t_1. In other words, for small σ_f values corresponding to the linear regime, this type of test is able to represent the isothermal or isochronal spectrum of the loss dynamic compliance. For obvious experimental reasons, it is difficult to carry out tests over several decades of time with the aim of describing the isothermal spectra. Consequently, most of this study is concerned with the description of isochronal spectra over a large temperature range, from −150 to 150°C, corresponding, therefore, to the frequency $N = 1/2\pi\tau_{moy}$, i.e. $1/2\pi t_1$ for $x = 5$. Moreover, in longitudinal solicitation, $J''(\tau) = E''(\tau)/(E''(\tau)^2 + E'(\tau)^2)$ and for every test condition the loss modulus $E''(\tau)$ is negligible when compared to the storage modulus $E'(\tau)$. Therefore, we can use $J''(\tau) = E''(\tau)/E'(\tau)^2$, and as the loss tangent $\tan\phi = E''/E'$ we can obtain the following expression, i.e. $J''(\tau) = \tan\phi(\tau)/E'(\tau)$. Furthermore, to a first approximation, we can use $E(t) = E'(\tau)_{\tau=t}$, and then deduce $E'(\tau)$ from measurement with an extensometer of the relaxed modulus $E(t)$, corresponding to the first stage of our test. Thus, we are also able to describe the dynamic spectrum, $\tan\phi(T)$, from the antistress relaxation results.

Finally, by using $x = 5$, we obtain the following expressions:

$$J''(\tau)_{\tau=t_1} = \frac{\pi}{2}\left(\frac{1}{1.22}\right)\left(\frac{1}{\sigma_f}\right)\left[\frac{\sigma_{ar}(5t_1)}{E_{ms}(5t_1)}\right] \tag{9}$$

$$\tan\phi(\tau)_{\tau=t_1} = \frac{\pi}{2}\left(\frac{1}{1.22}\right)\left(\frac{1}{\sigma_f}\right)\left[\frac{\sigma_{ar}(5t_1)}{E_{ms}(5t_1)}\right]E(t_1) \tag{10}$$

Comparison between the antistress relaxation test and mechanical spectrometry

To validate the above analysis, it is necessary to compare the dynamic spectra obtained from the antistress relaxation test, using small values of σ_f (linear regime), with those obtained from conventional mechanical spectroscopy[4,5] for an equivalent frequency. The results displayed in *Figure 7* exhibit a remarkable similarity between the J'' and $\tan\phi$ spectra, obtained from the two very different methods. Only small differences are observed, which could be due to several reasons:

(a) As seen previously, viscoelastic analysis of the antistress relaxation requires some approximations.
(b) The two types of test have not been performed on strictly the same materials.
(c) In order to be compared with data obtained by torsion dynamic spectroscopy, the results obtained from the antistress relaxation test have been corrected for shear by using a Poisson ratio of 0.35, assumed constant with temperature.
(d) The 10 MPa preload is not taken into account in the previous analysis.

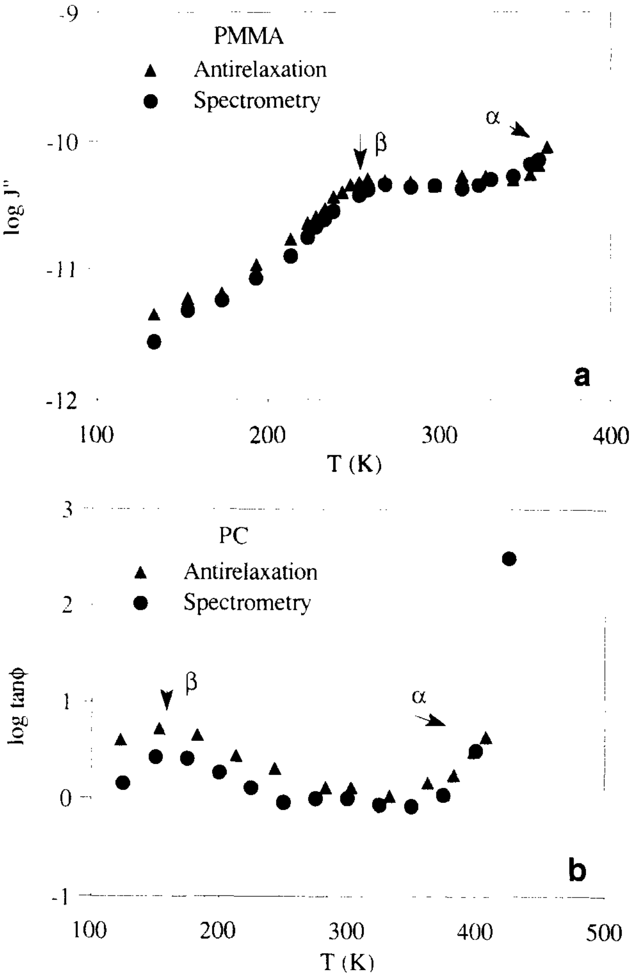

Figure 7 Comparison between the J'' isochronal spectra obtained with conventional mechanical spectroscopy and with the use of the antistress relaxation test (in the linear regime). (a) J'' spectra for PMMA: (▲) from antistress relaxation, with $t_1 = 4$ s and $\sigma_f = 30$ MPa; (●) from mechanical spectrometry[4], at a frequency of 5×10^{-2} Hz. (b) Tan ϕ spectrum for PC: (▲) from antistress relaxation, with $t_1 = 12$ s and $\sigma_f = 50$ MPa; (●) from mechanical spectrometry[5], at a frequency of 10^{-2} Hz

(c) σ_f is perhaps not small enough to clearly correspond to the linear regime.

However, it is worthwhile emphasizing the fact that these potential causes of errors are comparatively insignificant in view of the small discrepancies observed between the two spectra obtained by two, quite different methods.

Therefore, by both techniques and for two different materials, we can observe the β-relaxation at low temperatures and, at higher temperatures, the low-temperature part of the α-relaxation. In this linear regime, the highest temperature reached with the antistress relaxation test corresponds to the one above which the static preload produces a large plastic flow which prevents us from carrying out any measurements.

As a conclusion to this section, we can state that this original test, which is very different to the usual dynamic tests, is able to determine the isochronal dynamic spectrum. Obviously, in the linear regime, this new type of test is less accurate than the conventional dynamic mechanical method but, on the other hand, it does allow us to apply very large stresses and then to observe the non-linear behaviour of such anelastic properties.

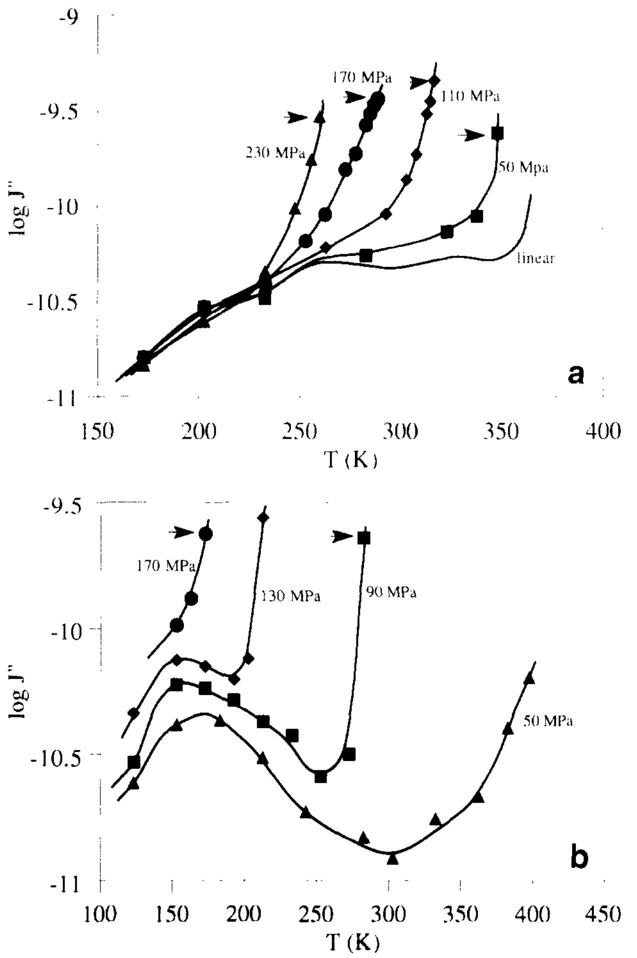

Figure 8 Extrapolated isochronal J'' spectra in the non-linear regime, obtained using the antistress relaxation test, showing the effect of variations in the maximum applied stress: (a) for PMMA, with $t_1 = 12$ s (the spectrum corresponding to the linear regime is deduced from *Figure 7a*); (b) for PC, with $t_1 = 12$ s. In all of the spectra the arrows correspond to the points obtained for experimental conditions leading to a plastic strain of ~ 1% after the test

Non-linear regime

Figure 8 shows changes to the spectra when the maximum applied stress increases. However, we must bear in mind that, in the non-linear regime, an analysis using linear viscoelastic equations and, in particular, the Boltzmann superposition principle, is no longer valid. Nevertheless, thanks to this extrapolated spectrum representation in the non-linear domain, we can observe the main trends and determine which is modified when the maximum applied stress is increased. Furthermore, we know from previous work[6] that in the non-linear domain, the actual recovery of the deformation is faster than that predicted by the Boltzmann superposition principle. Therefore, the antistress measured in the non-linear domain is also less significant than what it would be if the material behaviour followed this principle. Consequently, we can say that the J'' values obtained from the antistress relaxation measurements in the non-linear regime are underestimated with respect to previous analytical results, and consequently, the non-linear effects on J'' are also underestimated. Moreover, we have only presented the J'' spectrum, which, unlike $\tan\phi$, can be obtained without any measurement of $E(t)$ and therefore, any analogy with $E'(\tau)_{\tau=t}$, extrapolated in the non-linear regime, would be largely questionable.

We can observe in *Figure 8* a clear influence of the applied stress on the anelastic part of the α-relaxation[7]. In fact, this latter is shifted towards lower temperatures when σ_f increases and, for high stress levels, the β- and α-relaxation peaks merge together. We can also note that for a given σ_f value, the α-relaxation shift is more pronounced for PC than it is for PMMA. Finally, for a given σ_f increase, we can observe that the α-shift seems to slow down at the approach of the β-relaxation peak.

Dynamic torsion tests carried out on epoxy resins have shown[8] that an increase in the applied stress leads to a shift of the whole α-relaxation peak in the $\tan\phi$ spectrum towards lower temperatures. These results therefore appear to confirm our observations.

On the other hand, the experimental accuracy does not allow us to detect a very clear effect of the applied stress on the β-relaxation at low stress levels; moreover, for higher stress levels, the α- and β-relaxations merge. However, in the case of polycarbonate, it seems that the β-peak exhibits a slight shift towards the low temperature region and also a slight increase in height. This increase could be at least partly due to the α-relaxation shift towards low temperatures, whereas the shift towards low temperatures of its maximum cannot be due, in any case, to this α-shift, since such a shift towards low temperatures with a fixed β-peak, would lead to an apparent displacement of the maximum of the β-peak towards the high temperature region.

The experimental points obtained at the highest temperatures in each spectrum, in the vicinity of yield flow, show that the important non-linear strain which is usually observed at all temperatures just before the yield point, is mainly due to a dramatic increase in the anelastic strain which is thermomechanically activated. They also show that this important non-linear anelasticity which is observed just before yield is mainly due to the low-temperature part of the α-relaxation and therefore to molecular processes which are more complex than the simple one responsible for the β-relaxation. As this dramatic increase in the non-linear anelasticity always occurs near the yield flow point, we can assume that the molecular processes leading to this important macroscopic anelastic strain and the one leading to plastic flow are not independent. Therefore, it is not surprising to observe that the difference between PC and PMMA concerning the shift of the α-relaxation with σ_f is similar to that which has been previously observed for the evolution of yield stress with temperature[9]. Indeed, for a given applied stress increase, the corresponding decrease in the yield temperature is also more significant for PC than for PMMA.

In the following discussion, we will consider, using the time–temperature equivalence, that the observed changes due to the effects of the stress must be the same in both the isochronal and the isothermal J'' spectra. Furthermore, we will use the fact that the trends indicated in the isothermal J'' spectrum should also be observed in the relaxation time spectrum.

We can thus assert that the applied stress increase leads to a decrease in the characteristic times of the anelastic component of the α-processes. However, it is difficult to find clear evidence for a decrease in the β-relaxation characteristic times. Therefore, we can say that the stress has a more important effect on the characteristic times of the α-processes than on those of the β-processes.

Unfortunately, it is also difficult to determine any clear trend corresponding to the stress effect on the amplitude of the two relaxations. For α-relaxation, we must realize that the apparent shift observed towards smaller characteristic times could be due to an actual shift which is less important, but is combined with an increase in amplitude. For β-relaxation, the decrease of the α-relaxation times prevents us from asserting that the apparent increase of the β-peak is really due to an increase in the β-relaxation amplitude.

These two possible effects of the applied stress on the α- and β-relaxations, i.e. a decrease in the characteristic times and an increase in the amplitude, could explain the macroscopic non-linear behaviour observed in creep experiments. Thus, it is not surprising to note that most descriptions of non-linear behaviour tend to consider one or both of these two effects. In the following discussion, we will examine some of these descriptions and in addition we will try to propose a link between the anelastic α-processes and the yield processes since they do not appear to be independent of each other.

DISCUSSION

Non-linear anelasticity in the β-range

From the preceding results, it appears that for experiments involving creep measurements made at temperatures much lower than T_g, and under conditions of time and stress corresponding to linear or weakly non-linear behaviour, the observed macroscopic strain is mainly related to the β-motions.

To describe this weakly non-linear anelasticity, two effects of the stress increase have been proposed:

(1) An increase of the equilibrium anelastic compliance[10,11] ($J_{\mathrm{aneq}} = J_{\mathrm{an}}(t)$ when $t \to \infty$).
(2) A rheologically simple shift of the characteristic times[12] (i.e. a shift conserving the spectra shape) towards lower values.

In the J'' spectra, an increase of the J_{aneq} values corresponds to an increase in the values of J''. On the other hand, a rheologically simple shift of the characteristic times corresponds to a horizontal translation of the whole J'' spectrum.

According to our results, the stress effect on the β-relaxation is not clearly defined. Thus, regarding the two effects proposed above to describe the weak non-linearity corresponding mainly to the β-processes, it is difficult to determine which of these is the more effective one. However, these results do show clearly that the stress effect on the whole J'' spectrum is neither a simple horizontal shift nor a vertical one. Consequently, the large non-linear anelasticity observed just before yield cannot be described by considering only one of these two effects.

In the following part of this discussion, we will present some works with a view to putting forward a physical explanation, and possibly a behaviour law, for this important non-linear anelasticity.

Non-linear anelasticity in the α-relaxation range

As stated above, these anelastic α-processes which lead to an important recoverable strain, also appear to be related to those leading to plastic flow, i.e. to an irreversible deformation. Indeed, whatever the temperature for our range of study, this important anelasticity is always present just before yield and consequently, similar to that of the yield processes, the anelastic α-processes imply a thermomechanical activation: the corresponding characteristic times decrease when the applied stress increases. It is therefore an interesting exercise to examine some of the physical descriptions proposed for these two types of processes.

Bowden and Raha[13] use the dislocation concept to describe the yield process, and calculate the thermal energy necessary for the nucleation of a sheared region ('dislocation loop') under a given applied stress, thus leading to plastic strain.

Moreover, in order to describe the important shear-recoverable strain observed at the yield point for PMMA at 20°C, they suggest that in many regions of the material a local yield can occur under a stress below that necessary for general yield strain. Furthermore, it is assumed that these regions, unlike the sheared regions formed at the yield point, cannot grow because of the back-stresses in the surrounding matrix; on unloading, such back-stresses would cause these regions to eventually move back to their original configurations.

It appears then that with this rather qualitative explanation, these authors assume that the molecular processes generating the irreversible strain and those generating the recoverable strain are fully independent of each other. In addition, they do not try to describe the effect of the applied stress on the anelastic processes.

In metallic glasses, Argon and Shi[14] consider that an isolated mechanical polarization or shear transformation can occur under stress in the microscopic volume elements having the lowest free energy barrier. They suggest then that the transformation gradually spreads at a decreasing rate to elements with increasingly large energy barriers. As long as each of these transformed volume elements is spatially isolated, the corresponding deformation is entirely anelastic. Indeed, on unloading, the back-stresses due to the elastic surroundings provoke a reverse shear transformation in every transformed volume element, and the sample returns completely to its initial shape. However, when some of these transformed volumes become adjacent to each other, the local back-stresses of such a cluster can be relieved. The 'memory' of the initial unstressed state becomes lost, and the observed strain is then irreversible. These authors also describe the anelastic processes as being the precursors of the yield processes. Nevertheless, they do not extend such an approach to glassy polymers and, anyway, no interpretation of the stress effect on these anelastic processes is given.

For their molecular model, Perez and coworkers[15-17] use, among others, concepts quite similar to those mentioned above, to describe the inelastic deformation of amorphous polymers. In short, it was assumed that in amorphous solids, there are microregions of the material corresponding to microfluctuations of density, which are called 'quasi point defects' (QPDs). In some of these defects, shear microdomains (SMDs) could be thermomechanically activated: the expansion of these SMDs occurs, then, as the result of hierarchically correlated molecular movements. In the case of polymers, such movements imply elementary molecular motions corresponding to conformational changes with a characteristic time, assumed to be identified as that of the β-relaxation.

This model then suggests that, under stress, the SMDs, which are bordered by a dislocation (a Somigliana one in the case of amorphous polymers[18]), can grow by a succession of correlated elementary β-motions. This growth corresponds to anelastic strain, since the elastic energy of the borderline forces these sheared regions to return to their initial unstressed states when the stress is removed. Finally, when the SMDs are very close, they 'coalesce', thus annihilating their borderline elastic energy, which leads then to an irreversible shear strain.

Therefore, from the single conformational change (typically a β-process) to the more complex molecular movement implying the coalescence of the SMDs (maximum α-relaxation), there is a continuously increasing development of a SMD-determining J'' spectrum between T_β and T_α.

With such a description, we notice that the characteristic times corresponding to the SMD growth, i.e. to the anelastic α-processes, are distributed between τ_β (the easiest nucleation) and $\tau_{\max}$ (coalescence). Moreover, an expression giving an account of the correlated effects has been proposed as follows:

$$\tau_{\max}(\sigma)=\left[\frac{\tau_\beta(\sigma)}{t_0^{1-\kappa}}\right]^{1/\kappa} \qquad (11)$$

where τ_β depends on both T and σ, due to the thermomechanically activated nature of the β-motion, t_0 is a constant scaling time parameter, and κ is the correlation parameter ($0<\kappa<1$).

The deduced α-anelastic compliance expression is then as follows:

$$J_{\mathrm{an}\alpha}(t)=J_{\mathrm{an}\alpha\mathrm{eq}}\sum_i \frac{g_i}{\sum_i g_i}\left[1-\exp\left(-\frac{t}{\tau_i(\sigma)}\right)\right] \qquad (12)$$

where g_i are linear parameters, and $\tau_i(\sigma)$ are times distributed from $\tau_\beta(\sigma)$ to $\tau_{\max}(\sigma)$.

Consequently, all of the characteristic times $\tau_i(\sigma)$ corresponding to various states of growth of the SMDs up until coalescence occurs, are shorter when the stress is high. Moreover, in this model, the stress effect is all the more important as τ is high and does not lead to a rheologically simple shift of the characteristic times. This agrees with our results, since the J'' shift is particularly important when the temperature is high.

With the above expression, it has been possible to describe[19,20], at least semiquantitatively, the creep, and also the recovery behaviour, of several polymers over a large range of temperatures, times and stresses. However, in a recent work on poly(vinyl chloride)[21], it appears that a quantitative description of the non-linear creep and recovery near the glass transition needs to consider the effect of the stress on the equilibrium α-anelastic compliance, $J_{\mathrm{an}\alpha\mathrm{eq}}$.

Energy profile

From the theory described above, concerning the molecular processes occurring in QPDs which lead to anelastic/plastic deformation, we can try to represent, at least qualitatively, the energy profile[22] corresponding to the energy state of a microregion in which a SMD is nucleated and then expands.

For this purpose, the usual calculation of the energy of a dislocation loop is carried out by considering:

(1) the elastic energy of the strain field of the dislocation, which is given by the following expression:

$$2\pi R\frac{Gb^2}{4\pi}\ln\left(\frac{2}{\sqrt{3}b}R\right) \qquad (13)$$

where G is the shear modulus, b is the Burger vector and R is the dislocation loop radius;

(2) the work done by the applied stress, i.e. $\pi R^2\tau b$ (τ = applied shear stress).

Let us apply such a result to the Somigliana dislocation loop bordering a SMD. In *Figure 9a*, with $b=4\times10^{-10}$ m and $G=2\times10^9$ Pa, we can see the energy profiles obtained for several values of the stress, with only the above two considerations taken into account. These profiles can be compared to those calculated by Bowden and Raha[13].

However, in addition, we must take into account further considerations:

(1) For a shear microdomain (SMD) with a radius smaller than a certain value ($\sqrt{3}b/2$), corresponding to the core of the associated dislocation, there is no elastic energy.

(2) The average size of the SMDs just before their coalescence could be compared to the distance between two activated QPDs, so that this can be estimated to have a value of ~3 nm (i.e. the radius is close to $4b$). These values can be obtained by considering that only the most disordered sites (i.e. only a minor fraction of the QPDs) are activated. Moreover, this value of the distance is comparable with the 'plastic-event size', suggested by molecular simulation on glassy polymers[23].

Beyond this critical size, the annihilation of the dislocation elastic energy ought to occur on a distance which is more or less comparable to the core of this

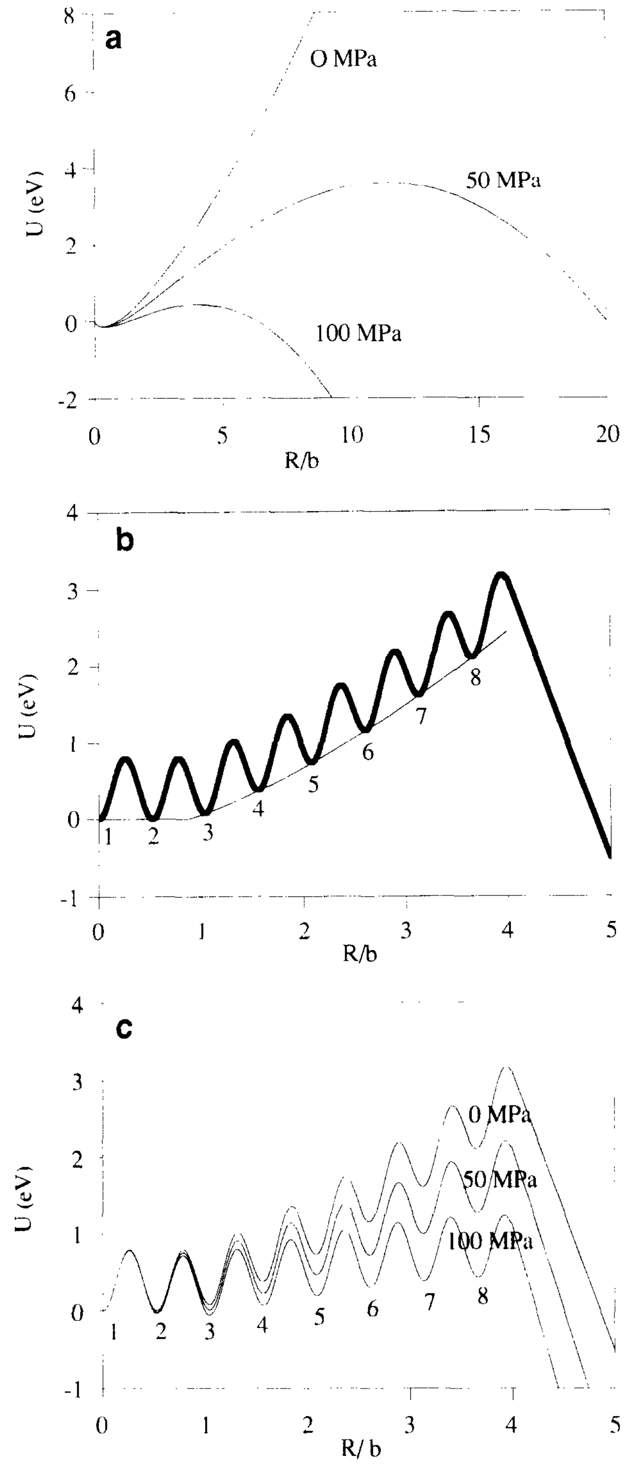

Figure 9 (a) Energy profiles of a dislocation for three different applied stresses, deduced from the usual calculation, i.e. considering only the elastic energy of the dislocation and the work done by the applied stress. (b) Energy profile with no applied stress, obtained by taking into account other considerations corresponding to the SMD core, growth and coalescence. The energy barriers are associated with conformational changes. (c) Influence of applied stress on the profile shown in (b)

dislocation. On the energy profile, this annihilation is depicted by an energy decrease until a value of zero is reached, which occurs over a distance which is approximately equal to b.

On such an energy profile, we must add a succession of barriers corresponding to conformational changes, i.e. elementary β-motions assumed to be necessary for the SMD growth. Obviously, the energy height of these added barriers is similar to the activation energy of the β-process (0.78 eV for PMMA).

We next consider the curve (without any applied stress) which is presented in *Figure 9b*. This representation is semiquantitative since we have used realistic values of the different physical parameters to obtain it. However, the distance between two successive β-barriers is arbitrary; furthermore, with only one spatial coordinate, this simplified view does not take into account the fact that a motion leading to the SMD growth in the stress direction can be achieved only after the realization of other motions in the vicinity and in all directions in space. Nevertheless, as we shall see further, this representation does, in fact, allow us to describe, rather well, several other experimental observations.

With this type of representation, the energy state of an unactivated defect corresponds to the first well. Each of the other wells corresponds to a possible energy state for an activated defect (SMD) so that we can calculate its equilibrium population using Boltzmann statistics. Moreover, the height of the barriers corresponds to the amount of thermal energy (kT) for the passage from one state to another, and thus reflects the kinetics of such changes of energy state.

In *Figure 9c*, it can be seen that the whole energy profile 'sinks' with an increase in the applied stress. The two main consequences resulting from this are:

(1) The equilibrium population of every well is changed. Therefore, in order to be part of this new equilibrium, several defects must be activated and some of the pre-existing SMDs must grow.
(2) From a kinetic point of view, the passage from one energy state to another, corresponding to the growth of the SMD, will be as fast as the applied stress will be high. Indeed, the energy barrier heights, and above all, the ones corresponding to the achievement of a large SMD, decrease when the applied stress increases.

Consequently, it can be suggested that such an alteration in the energy profile results in a non-linear increase with stress of each equilibrium population of the activated states, and thus, of their strain components. This corresponds to an increase of the equilibrium α-anelastic compliance with the stress.

Concerning the plastic deformation, these representations show that, at low temperatures, under a low stress and over the usual time scale, the plastic deformation cannot occur since the growth kinetics of a SMD are then very slow. On the other hand, we can appreciate that when the temperature is raised, thus providing a greater amount of thermal energy, or when the applied stress increases, decreasing then the heights of the barriers, these kinetics become faster so that the plastic strain will correspond to shorter times. All these features are self-consistent with the thermomechanically activated nature of the anelastic and plastic deformation, and also agree with our experimental observations (see e.g. *Figure 5*).

Moreover, the main result deduced from the antistress relaxation test is that the α-process merges into a β-relaxation for high applied stress levels; this can be easily understood in terms of the above analysis. Indeed, at very high stresses, the amount of thermal energy necessary to go from well 1 to well 2, corresponding to a simple β-motion, is close to that required in order to pass from an unactivated QPD state (well 1) to any other state, even including the one corresponding to SMD coalescence, leading to irreversible or plastic strain. We can thus assume that the kinetics of these two types of motion are very similar, so that the β- and α-phenomena are expected to be observed together for high applied stresses. Furthermore, it is worthwhile pointing out that such a merger which, from the energy representation, occurs for shear stresses of ~100 MPa (i.e. 200 MPa in uniaxial stress), is quantitatively in agreement with our experimental results. On the other hand, under very high applied stresses, the β-motion still appears to be necessary in order to achieve plastic strain; this could explain why the shift of the α-anelastic component towards lower temperatures (or smaller times) seems to slow down at the approach of the β-relaxation.

Finally, Turner's observations[6] can also be explained: the energy barriers that need to be crossed in order for a SMD to grow are higher than those to be negotiated on its return to the initial state after stress removal (compare the 0 MPa curve to others in *Figure 9c*). Consequently, the rate of recovery of the anelastic strain is higher than the rate of the anelastic deformation.

The quantitative aspects of the above approach are now being developed; for this purpose, we are continuing our studies at both an experimental and a theoretical level.

REFERENCES

1 Sweeney, J. and Ward, I. M. *J. Mater. Sci.* 1990, **25**, 697
2 Ferry, J. D. 'Viscoelastic Properties of Polymers' Wiley, New York, 1980
3 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymers', Wiley, London, 1967
4 Muzeau, E. *PhD Thesis* INSA Lyon, 1992
5 Cavaille, J. Y. *PhD Thesis* INSA Lyon, 1987
6 Turner, S. in 'The Physics of Glassy Polymers' (Ed. R. N Haward), Applied Science, London, 1973, Ch. 3, p. 223
7 Cavaille, J. Y., Perez, J. and Johari, G. P. *Phys. Rev. (B)* 1989, **39**, 2411
8 Bruneau, P. and Merle, G. Personal communication
9 Bowden, P. B. in 'The Physics of Glassy Polymers' (Ed. R. N. Haward), Applied Science, London, 1973, Ch. 5, p. 279
10 Boyd, R. H., Robertsson, M. E. and Jansson, J. F. *J. Polym Sci. Polym. Phys. Edn* 1982, **20**, 73
11 Brueller, O. S. *Polym. Eng. Sci.* 1987, **27**, 144
12 Questad, D. L. *Polym. Eng. Sci.* 1986, **26**, 269
13 Bowden, P. B. and Raha, S. *Philos. Mag.* 1974, **29**, 149
14 Argon, A. S. and Shi, L. T. *Acta Metall.* 1983, **31**, 499
15 Perez, J. 'Physique et Mécanique des Polymères Amorphes', Lavoisier, Paris, 1992
16 Mangion, M. B. M., Cavaille, J. Y. and Perez, J. *Philos. Mag. A* 1992, **66**, 773
17 Perez, J. *Rev. Phys. Appl.* 1986, **21**, 93
18 Li, J. M. C. in 'Metallic Glasses', American Society for Metals, Ohio, 1978, p. 224
19 Boucquerel, F., Bourgin, P. and Perez, J. *Polymer* 1992, **33**, 516
20 Ouali, N., Mangion, M. B. M. and Perez, J. *Philos. Mag. A* 1993, **67**, 827
21 Ladouce, L. Personal communication
22 Perez, J. *J. Phys. Colloq.* 1983, **44**, c9, 3
23 Mott, P. H., Argon, A. S. and Suter, U. W. *Philos. Mag. A* 1993, **67**, 931