

Shear yielding threshold and viscoelasticity in an amorphous glassy polymer: a study on a styrene–acrylonitrile copolymer

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Abstract

The framework of the present research is the study of the effects of viscoelasticity on the yield behaviour of amorphous glassy polymers. The research regards the shear yielding mechanism in an amorphous glassy polymer and the identification of a yield criterion, which takes into account the effect of mechanical history on the yield point (defined as the onset of plastic strain), is set as its final goal. To this end, constant strain-rate, creep and stress relaxation tests were carried out at room temperature under uniaxial compression conditions on a styrene–acrylonitrile copolymer. The results obtained emphasise that yield onset cannot be identified by a critical value of the applied stress or strain. Referring to models of the plastic deformation mechanism previously proposed in the literature, the anelastic strain, the anelastically stored energy and the viscoelastic energy were suggested to reach a threshold value at the yield point. All three parameters were evaluated at the yield threshold and showed fairly constant values irrespective of the mechanical history. Nevertheless, the data dispersion and the simplicity of the analogical model used to estimate these quantities did not allow to identify which of them actually controls the yield process. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Yield criteria; Viscoelasticity; Uniaxial compression

1. Introduction

Up to date, the shear yield threshold for polymeric materials has been analysed mainly following two different approaches. The first is a continuum mechanics approach in which the yield criteria applied generally to metals have been adapted to polymeric materials taking into account their pressure sensitivity [1]. The second considers yielding from a molecular and structural point of view and in the present work the models proposed by Oleinik and co-workers [2–5] and Boyce and co-workers [6–8] will be considered. Some authors [1,9] have considered both approaches.

With regard to the first approach, the above-mentioned yield criteria seem to provide a rather good description of the yield threshold as a function of the stress state, but this has been verified only in constant strain-rate tests. The effect of loading history, related to the polymers' viscoelasticity, has not been studied widely. Some work has been done by Brüller [10,11], who proposed an energy-related failure theory that considers as a critical parameter, both for

shear yielding and crazing, the sum, W^{vc} , between the time-dependent part of the specific stored energy, W_1^e , and the specific dissipated energy, W^{diss} .

As for the second approach, following Oleinik et al. [2–5] the plastic deformation of an amorphous polymer in its glassy state consists of repeated local deformation processes. Local shear defects, (defined as plastic shear transformations, PSTs) begin to nucleate at the early stages of loading. An increase in material's internal energy and the formation of new PSTs with increasingly higher stored energy take place as the macroscopic deformation increases. The strain accumulated in the PSTs is frequently referred to as the anelastic component, ϵ_{an} , of the total strain, ϵ_{TOT} . When the local deformation and the local energy linked to PST reach high critical values, conformational rearrangements of short sequences of polymer chains occur in the core of the defect or in its neighbourhood, transforming the PST into conformational excited coils (CEC). The CEC formation is a defect relaxation process that allows the relaxation of the local energy excess, but preserves the local deformation. The strain connected with the CEC is frequently referred to as the plastic strain component, ϵ_{pl} , of the overall strain, ϵ_{TOT} , and it is thermally recovered only in the glass transition range. The anelastic strain component, ϵ_{an} , instead, is recovered largely at lower temperatures.

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It has to be remarked that in the glassy state CEC and thus plastic strain cannot form unless anelastic strain has been accumulated through PST nucleation. Moreover, in constant strain-rate tests, the anelastic strain continues to increase also when the total strain is beyond the yield point. ϵ_{an} will tend towards an asymptotic value, which is reached when the rates of PST nucleation and of their conversion into CEC equilibrate.

Hasan and Boyce [6,7] propose a slightly different approach to the description of the plastic process, in which local shear transformation events, like the PST, are still considered. They assume that, as strain increases, at a certain point the “matrix” material available for the strain energy storage for the shear transformation will be depleted. Additional energy can no longer be stored in the material by this mechanism. When this happens, further energy is stored in the material by the creation of new defects (high local free volume sites, the so called “soft” sites), which corresponds to the plastic strain formation. In the present work the energy stored through the mechanism of shear transformations will be defined as “anelastically stored energy” (W_1^e).

The aim of this paper is the study of yield onset dependence on loading history in an amorphous glassy polymer. Mechanical tests have been performed under different loading histories and the yield point determined for each one. The results obtained clearly show that yield onset cannot be determined simply by a critical value of stress or strain, since both depend on the loading history. Therefore, the identification of a yield criterion through the definition of a quantity, which, irrespective of the applied loading history, has a critical value at yield onset, was attempted. Referring to the above-quoted literature, the anelastic strain, ϵ_{an} , the anelastically stored energy, W_1^e , and the viscoelastic energy, W^{ve} , were considered as possible quantities critical at yield onset.

2. Experimental

2.1. Material

Testing was performed on a styrene–acrylonitrile copolymer having 33 wt% acrylonitrile and weight average molecular weight of 80000, provided by ENICHEM.

Its glass transition temperature ($T_g = 110^\circ\text{C}$) was determined by means of differential scanning calorimetry (DSC) at $20^\circ\text{C min}^{-1}$ heating rate. The secondary transition temperatures ($T_\beta = -30^\circ\text{C}$, $T_\gamma = -125^\circ\text{C}$) were determined from the dynamic mechanical experiments performed at 1 Hz and at a $20^\circ\text{C min}^{-1}$ heating rate [12].

2.2. Mechanical tests

Uniaxial compression tests were performed on cylindrical samples having 10 mm diameter and 10 mm height [7]. In order to minimise end-friction, sheets of polytetrafluoroethylene were used between the compression plates and

the sample surfaces [7,8]. Specimens were machined from plates compression moulded at 180°C and 5 MPa.

Before testing, the specimens were annealed in a vacuum oven for 4 h at 110°C and then for 1 h at 120°C . They were then cooled to 30°C in about 21 h and stored at 21°C for 24 h in a dry chamber. The treatment is performed in order to give the material a fixed microstructural state. Moreover, this treatment controls the water absorbed by the material, which, although modest, may affect its mechanical properties [12].

The tests were carried out at 21°C on a INSTRON 1185 equipped with a 100 kN load cell. During loading, sample deformation was measured by an extensometer fixed onto the two compression plates.

The residual strain in the samples after unloading was obtained as the relative variation of their height, h

$$\epsilon = \frac{h_0 - h}{h_0}$$

Height measurements were carried out with a micrometer.

The true stress, σ_T , was obtained from force, F , and strain, ϵ , measurements assuming a constant volume by the expression

$$\sigma_T = \frac{F}{A_0} (1 - \epsilon)$$

where A_0 is the initial specimen's cross-sectional area.

Three different mechanical histories were applied to the specimens:

1. constant strain rate;
2. constant load (creep);
3. constant displacement (stress relaxation).

Since it is not possible to apply an instantaneous load or displacement to a sample, constant loads for creep tests and constant displacement for stress relaxation tests were reached through a constant strain rate ramp at 0.5 min^{-1} .

2.3. Yield onset determination

For any mechanical history, the overall strain can be thought of as the sum of three contributions: an elastic, an anelastic and a plastic strain. By separating the overall strain into its components, the yield point, defined as the onset of plastic strain, can be determined. The elastic strain, ϵ_{el} , depends only on the momentary stress level and recovers instantaneously after unloading. The anelastic strain, ϵ_{an} , evolves with time (even under constant load or deformation conditions) and recovers as a function of time after unloading. The plastic strain, ϵ_{pl} , sets in only after some loading time and is permanent [1,4,6].

If a series of identical specimens are loaded up to different levels and then unloaded, yield onset can be determined (irrespective of the loading history) through a

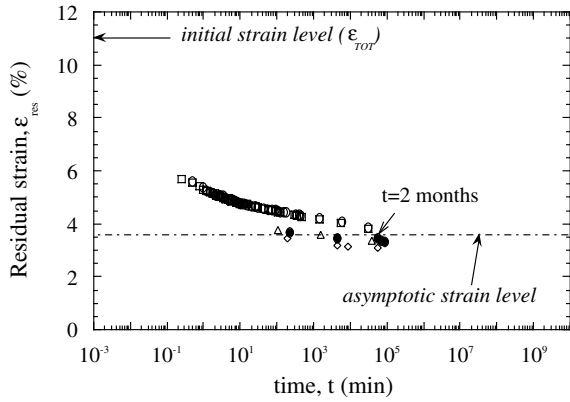


Fig. 1. Time-recovery of residual strain after unloading of samples initially deformed up to $\epsilon_{TOT} = 11\%$ through a loading ramp at $\dot{\epsilon} = 0.05 \text{ min}^{-1}$ ($T_{def} = T_{rec} = 21^\circ\text{C}$). Different symbols refer to different samples.

back extrapolation of the plastic strain versus total applied strain plot to zero value of ϵ_{pl} . This method, previously adopted in constant strain tests [1,9,13], has been adapted to the creep and stress relaxation experiments.

Since the elastic strain, ϵ_{el} , recovers during unloading, the residual strain, ϵ_{res} , after unloading is made of the anelastic component, ϵ_{an} , and, if the material has yielded, of the plastic component, ϵ_{pl} . The anelastic strain recovers with time and, therefore, the residual strain decreases with time towards an asymptotic value. This value is equal to zero or to ϵ_{pl} depending on whether yielding has occurred or not. In order to obtain ϵ_{pl} and correctly apply the extrapolation method, the anelastic strain component must always be totally recovered. Fig. 1 shows the residual strain as a function of time after unloading in samples previously deformed up to 11% strain at a constant strain rate of 0.05 min^{-1} . The decrease of ϵ_{res} with time is therefore due to the anelastic strain recovery and the asymptotic value is the plastic component. It is to be observed that, although most of the anelastic strain in the unloaded sample is recovered in a short time, the exact time necessary to reach the asymptotic value is not easily determined.

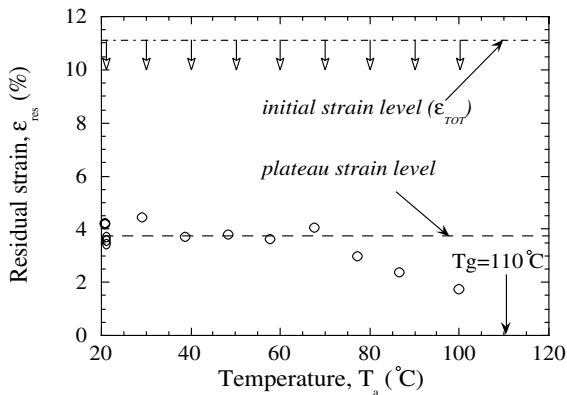


Fig. 2. Residual strains after 24 h as a function of annealing temperature (T_a). Before annealing, the samples were deformed up to $\epsilon_{TOT} = 11\%$ through a loading ramp at 0.05 min^{-1} and then unloaded.

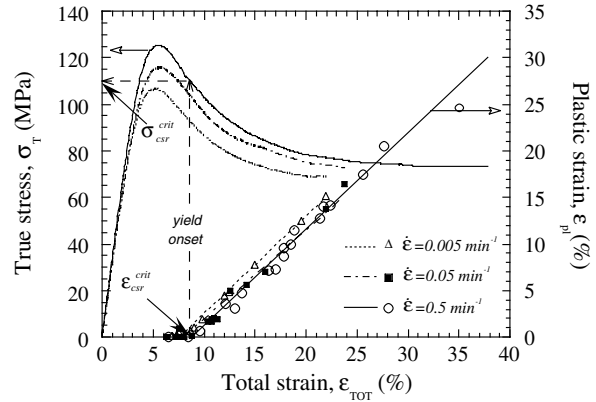


Fig. 3. True stress–strain curves at different strain rates together with the relevant ϵ_{pl} vs ϵ_{TOT} plots. The yield onset ($\epsilon_{0.5}^{crit}$, $\sigma_{0.5}^{crit}$) determination for $\dot{\epsilon} = 0.5 \text{ min}^{-1}$ is shown.

A thermal treatment may be applied to ensure the total recovery of the anelastic strain without altering the plastic strain. In order to determine the temperature and the duration of such a treatment, different specimens were deformed, as above, at 0.05 min^{-1} up to 11% strain and, after unloading, each sample was annealed for 24 h at a temperature T_a ($T_{def} = 21 \leq T_a < T_g = 110^\circ\text{C}$). Fig. 2 shows the residual strain, ϵ_{res} , as a function of T_a . The presence of a plateau in the temperature range from 30 to 70°C can be noticed. The residual strain plateau value is comparable to the asymptotic value obtained in the time–deformation–recovery at 21°C (Fig. 1).

Referring to these results and to the literature [13], in the present work a thermal treatment of 24 h at 60°C was adopted to totally recover the anelastic component of deformation.

2.4. Deformation components determination

After the yield onset determination, it is possible to obtain the values of the three components of the total strain, $\epsilon_{TOT} = \epsilon_{el} + \epsilon_{an} + \epsilon_{pl}$, at any time during a test according to the following equations:

$$\epsilon_{el} = \frac{\sigma_T}{E_{un}}, \quad \epsilon_{an} = \epsilon_{TOT} - \epsilon_{el} - \epsilon_{pl} = \epsilon_{TOT} - \frac{\sigma_T}{E_{un}} - \epsilon_{pl} \quad (1)$$

in which ϵ_{pl} is experimentally measured, σ_T is the true applied stress and E_{un} is the unrelaxed modulus, that is the material's modulus measured at very low temperature or

Table 1
Strain, stress and time to reach yield onset in constant strain rate tests

$\dot{\epsilon}$ (min^{-1})	ϵ_{csr}^{crit} (%)	σ_{csr}^{crit} (MPa)	t_{csr}^{crit} (s)
0.005	7.5	99 ± 1	984 ± 6
0.05	8.0	107 ± 5	100 ± 10
0.5	8.5	113 ± 7	11 ± 1

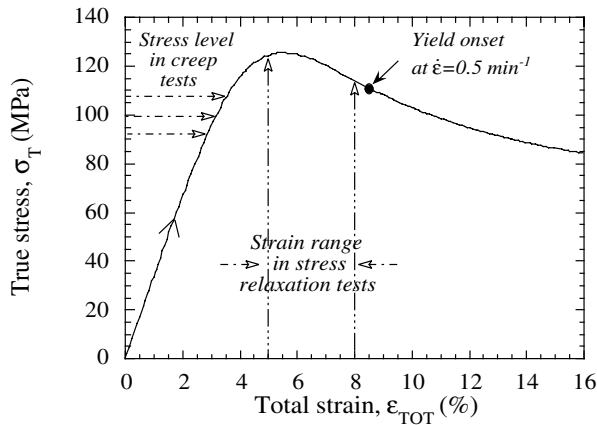


Fig. 4. Stress levels and strain range applied in creep and stress relaxation tests, reached through a loading ramp at $\dot{\epsilon} = 0.5 \text{ min}^{-1}$. The yield onset ($\epsilon_{0.5}^{\text{crit}}$, $\sigma_{0.5}^{\text{crit}}$) in the constant strain rate test at 0.5 min^{-1} is also shown.

high frequency. In this work a value of 6.1 GPa obtained in Ref. [12] from dynamic-mechanical measurement at 1 Hz and -150°C was used.

3. Results

3.1. Constant strain rate tests

Three different strain rates have been examined ($\dot{\epsilon} = 0.005, 0.05$ and 0.5 min^{-1}). The yield onset was determined, at each strain-rate, as follows. A series of identical samples were deformed up to different strain levels and heat treated after unloading as described above. Fig. 3 shows the stress–strain curves together with plastic strain versus applied strain plots obtained. By extrapolating the plastic strain to $\epsilon_{\text{pl}} = 0$, stress and strain at the yield point (σ^{crit} , ϵ^{crit}) were determined. In Table 1 σ^{crit} , ϵ^{crit} and time to yield (t^{crit}) are reported. It can be observed that: (i) for all strain rates, yield onset occurs beyond the maximum stress; (ii) the stress values at the yield point depends on the strain rate; (iii) strain at yield does not vary significantly with the strain rate. From these results it can be deduced that stress is not critical at yield.

3.2. Creep tests

A series of identical samples were loaded up to a fixed level of load through a constant strain-rate ramp at 0.5 min^{-1} after which the load was maintained constant for different creep times ($10^2 < t_{\text{creep}} < 10^5 \text{ s}$). The specimens were then unloaded and thermally treated to recover the anelastic component of deformation. Three different load levels at the end of the loading ramp, corresponding to true stresses of 92, 99 and 108 MPa, were considered. The ramp was always arrested before reaching the maximum stress in the relevant constant strain-rate test performed at the same rate as the loading ramp (Fig. 4).

In Fig. 5 the plastic deformation is reported as a function

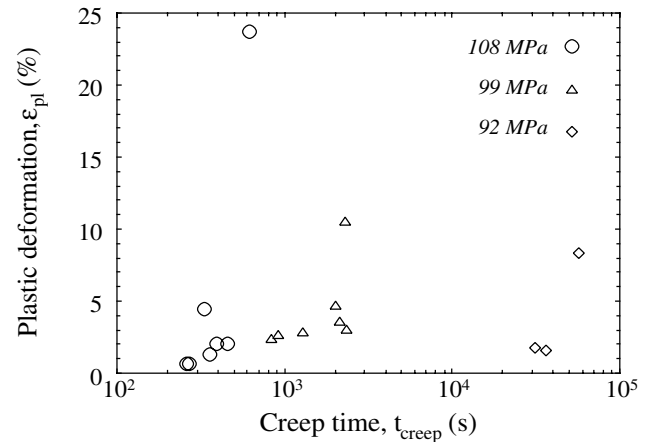


Fig. 5. Plastic strain as a function of creep time (t_{creep}) for samples loaded up to different levels of the initial true stress ($\sigma_T = 92, 99$ and 108 MPa).

of the creep time for each of the three stress levels. It can be observed that a 10% variation of the applied load shifts substantially the yield process on the time scale but, since data scattering is quite large, an extrapolation to obtain a creep time for zero plastic strain is difficult. Plastic strain was thus plotted as a function of total strain ϵ_{TOT} (Fig. 6) and the total strain value at yield onset obtained by extrapolation to $\epsilon_{\text{pl}} = 0$. Results are shown in Table 2. Within the experimental error yield strain is independent of the applied stress. Using an average value of yield strain, $\bar{\epsilon}_{\text{creep}}^{\text{crit}} = 7.8\%$, a yield time ($t_{\text{creep}}^{\text{crit}}$), defined as the time required to reach the yield point from the end of the loading ramp, was determined. This time is also reported in Table 2, for each of the applied stress levels. Creep tests show that stress is not critical at the onset of yielding, in agreement with constant strain-rate tests results.

3.3. Stress relaxation tests

A series of identical samples were loaded up to different strain levels (5.0, 6.0, 7.0, 7.4 and 8.0%) applied through a

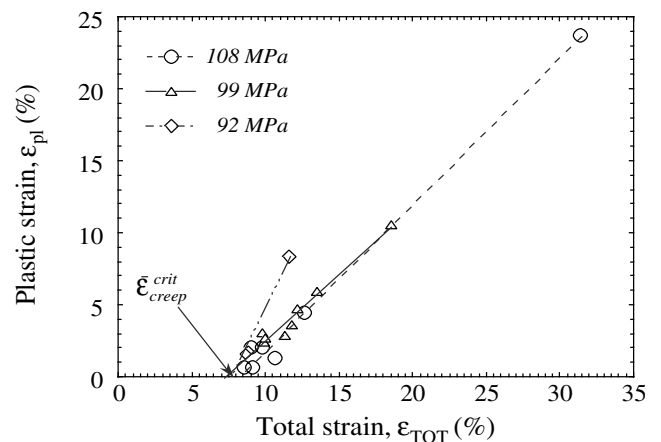


Fig. 6. Plastic strain as a function of total strain (ϵ_{TOT}) for the same samples as in Fig. 5.

Table 2

Strain at yield onset and time to reach the yield point from the end of the loading ramp in creep tests

σ_T (MPa)	$\epsilon_{\text{creep}}^{\text{crit}}$ (%)	$t_{\text{creep}}^{\text{crit}}$ (s)
92 ± 1	8.0	$(4 \pm 1) \times 10^4$
99 ± 3	7.3	$(2 \pm 1) \times 10^3$
108 ± 3	8.2	$(4 \pm 1) \times 10^2$

constant strain rate ramp at 0.5 min^{-1} , the stress was then allowed to relax for different times ($1 < t_{\text{rel}} < 7 \times 10^3 \text{ min}$). After unloading, the specimens were thermally treated before measuring the plastic strain. Even though the applied strains were always below the yield strain (8.5%) determined in the constant strain-rate test performed at the same rate as the loading ramp (Fig. 4), plastic deformation set in, indicating that the overall strain level is not a threshold for yielding.

In Fig. 7 the plastic strain values are shown as a function of the relaxation time, t_{rel} , for the different applied strains, ϵ_{TOT} . The data points available for the strain level of 8% were considered not sufficient for further elaboration. An empirical fit of the data relevant to the strain levels of 5.0, 6.0, 7.0 and 7.4% was performed using logarithmic functions. These functions were utilised to obtain, by extrapolation to $\epsilon_{\text{pl}} = 0$, the yield time (relaxation time at yield, $t_{\text{rel}}^{\text{crit}}$). From this time the stress at yield onset, $\sigma_{\text{rel}}^{\text{crit}}$, was determined. Table 3 reports the obtained yield stress and yield time values. Presumably the yield time for the strain 7.4% is affected by a large experimental error, due to the scarce experimental data at this strain level. In Fig. 8 yield time is plotted versus the applied strain. The strain value at yield onset obtained in the constant strain-rate test at the same rate as the loading ramp should correspond to a zero value of the yield time. This strain value (8.5%) is also reported in Fig. 8 and it appears consistent with the relaxation tests results.

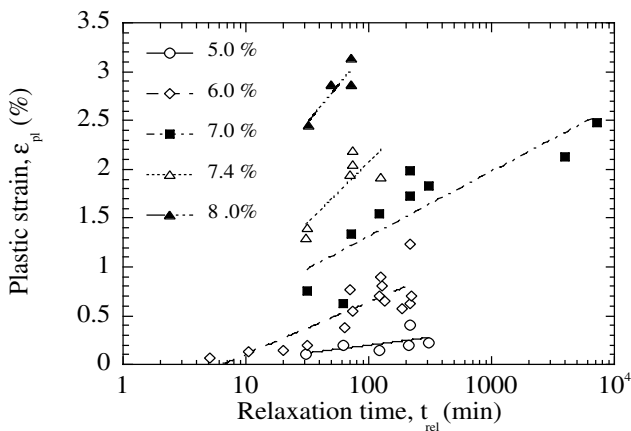


Fig. 7. Plastic strain as a function of relaxation time (t_{rel}) for samples deformed up to different strain levels ($\epsilon_{\text{TOT}} = 5.0, 6.0, 7.0, 7.4$ and 8.0%). Lines are logarithmic interpolation through all points.

4. Discussion

A schematic description of the mechanical tests performed and the relevant observations made on the results is:

Test	Applied loading	At yield onset
Constant strain rate (csr)	$\dot{\epsilon} = 0.005, 0.05$ and 0.5 min^{-1}	$\sigma_{\text{csr}}^{\text{crit}} = f(\dot{\epsilon})$ $\epsilon_{\text{csr}}^{\text{crit}} \approx \text{const}$, \rightarrow applied stress is not critical
Creep after loading ramp at 0.5 min^{-1}	$\sigma_{\text{creep}} = 92, 99$ and 108 MPa	$\epsilon_{\text{creep}}^{\text{crit}} \approx \text{const} \rightarrow$ applied stress is not critical
Stress relaxation after loading ramp at 0.5 min^{-1}	$\epsilon_{\text{rel}} = 5.0, 6.0,$ $7.0,$ and 7.4%	$\sigma_{\text{rel}}^{\text{crit}} = f(\epsilon) \rightarrow$ applied stress and overall strain are not critical

The constant strain rate experiments clearly show that stress is not the parameter that reaches a critical value at yield onset. This result is confirmed by creep and stress relaxation experiments. From the latter, it is also possible to state that strain too is not critical at yield onset.

Therefore, as mentioned in the introduction, the following three quantities were considered as potential parameters reaching a critical value at the yield point:

1. anelastic strain, ϵ_{an} , according to Oleinik and co-workers' description of the plastic process;
2. anelastically stored strain energy, W_1^{e} , following Boyce and co-workers' approach;
3. viscoelastic energy, $W^{\text{ve}} = W_1^{\text{e}} + W^{\text{diss}}$, in relation to Brüller results.

Up to yield the anelastic strain component can be directly determined from the relevant experimental applied stress and overall strain, using Eq. (1) with $\epsilon_{\text{pl}} = 0$:

$$\epsilon_{\text{an}} = \epsilon_{\text{TOT}} - \epsilon_{\text{el}} = \epsilon_{\text{TOT}} - \frac{\sigma_T}{E_{\text{un}}} \quad (2)$$

As for the two energies considered, they were estimated referring to the simple analogic Zener model (Fig. 9), which may, in a first approximation, describe the behaviour of a viscoelastic material before plastic deformation sets in.

The spring having elastic constant E_0 describes the pure elastic behaviour of the material and the parallel system, made of a spring having elastic constant E_1 and a dashpot having viscosity η_1 , is considered to describe the material's anelastic behaviour. The energy stored in the E_1 spring is therefore the anelastically stored energy W_1^{e} :

$$W_1^{\text{e}} = \frac{1}{2} \epsilon_{\text{an}}^2 E_1 = \frac{1}{2} (\epsilon_{\text{TOT}} - \epsilon_{\text{el}})^2 E_1 = \frac{1}{2} \left(\epsilon_{\text{TOT}} - \frac{\sigma_T}{E_0} \right)^2 E_1 \quad (3)$$

The viscoelastic energy W^{ve} is given by the simple equation:

$$W^{\text{ve}} = W_{\text{TOT}} - W_0^{\text{e}} \quad (4)$$

Table 3

Stress at yield onset and time to reach the yield point from the end of the loading ramp in stress relaxation tests

ϵ (%)	σ_{rel}^{crit} (MPa)	t_{rel}^{crit} (s)
5.0 ± 0.1	85 ± 2	350
6.0 ± 0.4	82 ± 3	180
7.0 ± 0.3	80 ± 1	60
7.4 ± 0.1	69 ± 1	130

in which W_{TOT} is the deformation work:

$$W_{TOT} = \int_0^\epsilon \sigma_T d\epsilon \quad (5)$$

and W_0^e is the elastically stored energy in the spring E_0 :

$$W_0^e = \frac{1}{2} \frac{\sigma_T^2}{E_0} \quad (6)$$

For E_0 , the value of the unrelaxed modulus (6.1 GPa) was used [12].

As for the modulus E_1 , whose value is related to the relaxation process involved in the plastic strain, the material's rubbery plateau modulus ($E_1 = 1.26$ MPa [14]) was at first considered, since the thermal recovery of plastic strain takes place above the glass transition temperature. Using these values for E_0 and E_1 and the experimental value of the applied stress, by combining Eqs. (3) and (6), the total stored energy ($W_0^e + W_1^e$) was calculated at yield onset ($\epsilon_{TOT} = 8.5\%$) for the constant strain rate test at 0.5 min^{-1} and resulted to be ~ 1 kJ/kg. This value is quite different from the total stored energy value of 5.3 kJ/kg determined by Oleinik [15] at a similar strain (10%) in a deformation calorimetry test performed at similar strain rate (0.1 min^{-1}). In this test the total stored energy is evaluated as the difference between the deformation work and the heat (corresponding to the dissipated energy) directly measured during the experiment.

Oleinik's value of total stored energy was then used to

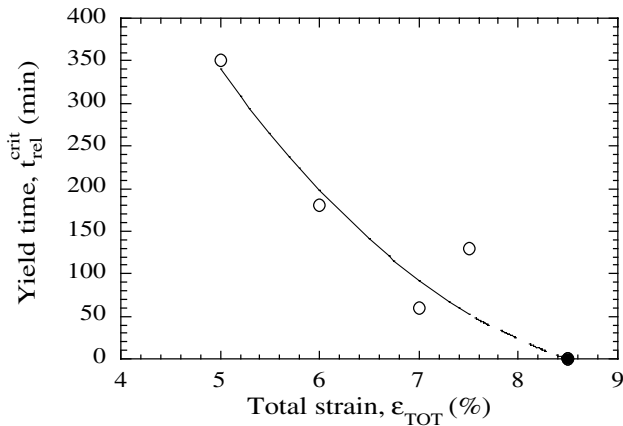


Fig. 8. Yield time (t_{rel}^{crit}) as a function of the applied strain (ϵ_{TOT}) in stress relaxation tests. The full point is the yield onset in 0.5 min^{-1} constant strain-rate test (see text).

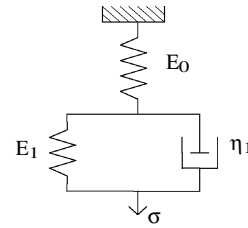


Fig. 9. Zener model.

estimate, through the Eqs. (3) and (6), the modulus E_1 which turned out to be 1.49 GPa. This value is comparable with the material's modulus measured by means of dynamic mechanical experiments [12] after the activation of γ and β relaxations.

Since this result is in agreement with Refs. [4,5] where it is suggested that the molecular relaxations related to the formation of PST, which precedes the yield process, are correlated to β and γ motions, in the following the value of 1.49 GPa was used for the modulus E_1 .

Table 4 reports, for each of the applied loading histories, the values at yield onset of the anelastic strain together with the anelastically stored energy and the viscoelastic energy. It can be observed that in the stress relaxation tests, the values obtained for each of the three parameters are systematically lower than those obtained in the other tests. This is probably due to the empirical method adopted for yield onset extrapolation.

Notwithstanding the scattering of the data obtained, an attempt to evaluate if one of these parameters is critical at yield onset was performed, examining their constancy irrespective of the loading history. To this purpose, the mean value, X_m , of each of the three parameters was evaluated considering all the loading histories. They are reported in Table 4 together with their coefficient of variation, V . Moreover, the difference, ΔX , between the parameter's value determined in a single loading history and its mean value, X_m , was calculated. The ratio between ΔX and X_m is shown in Fig. 10 for all the parameters and for each of the applied loading histories. The figure qualitatively shows that

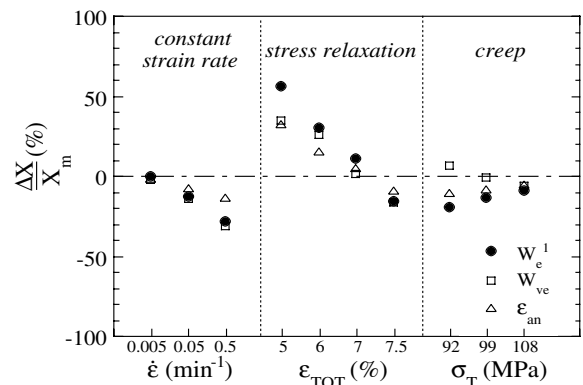


Fig. 10. Deviation of W_1^e , W^{ve} and ϵ_{an} from their mean value for all loading histories.

Table 4

Anelastic strain component (ϵ_{an}) anelastically stored energy (W_1^e) and viscoelastic energy (W^{ve}) at yield onset for each of the performed loading histories, together with their mean values (X_m) and coefficients of variation (V)

Test	Test condition	ϵ_{an} (%)	W_1^e (kJ/kg)	W^{ve} (kJ/kg)
Constant strain rate	$\dot{\epsilon} = 0.005 \text{ min}^{-1}$	5.9 ± 0.1	2.6 ± 0.1	5.2 ± 0.1
	$\dot{\epsilon} = 0.05 \text{ min}^{-1}$	6.3 ± 0.1	3.0 ± 0.1	6.0 ± 0.2
	$\dot{\epsilon} = 0.5 \text{ min}^{-1}$	6.6 ± 0.3	3.3 ± 0.1	7.0 ± 0.1
Creep	$\sigma_T = 92 \text{ MPa}$	6.4 ± 0.1	3.0 ± 0.1	4.9 ± 0.1
	$\sigma_T = 99 \text{ MPa}$	6.3 ± 0.1	2.9 ± 0.1	5.3 ± 0.1
	$\sigma_T = 108 \text{ MPa}$	6.1 ± 0.1	2.8 ± 0.1	5.6 ± 0.1
Stress relaxation	$\epsilon_{TOT} = 5.0\%$	3.9 ± 0.5	1.1 ± 0.1	3.4 ± 0.1
	$\epsilon_{TOT} = 6.0\%$	4.9 ± 0.5	1.8 ± 0.3	4 ± 1
	$\epsilon_{TOT} = 7.0\%$	5.5 ± 0.3	2.3 ± 0.3	5.2 ± 0.4
	$\epsilon_{TOT} = 7.4\%$	6.3 ± 0.1	3.0 ± 0.1	6.1 ± 0.1
Mean value, X_m		5.8	2.6	5.3
Coefficient of variation, V (%)		15	25	20

the anelastic strain seems to deviate less from its mean value than the other two quantities. The result is confirmed by the values of the coefficients of variation.

5. Conclusions

Yield onset dependence on loading history in an amorphous glassy polymer was studied and several quantities were considered as possible critical parameters at the yield point. It turned out that yield onset cannot be simply determined by a critical value of the overall stress or strain, since they both depend on the mechanical history. The other three quantities considered, the anelastically stored energy, the viscoelastic energy and the anelastic strain, are fairly constant at yield onset irrespective of loading history, even if the latter shows a lower variability.

A better modelling of the deformation process both before and after the onset of plastic deformation should allow a more accurate data handling for yield onset determination and a more precise evaluation of the above mentioned quantities. Further work in this direction is under way in order to identify which parameter actually controls yield onset.

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References

- [1] Quinson R, Perez J, Rink M, Pavan A. *J Mat Sci* 1996;31:1–9.
- [2] Oleinik EF. *Progr Coll Polym Sci* 1989;80:140–50.
- [3] Rudnev SN, Salamatina OB, Voenny VV, Oleinik EF. *Colloid Polym Sci* 1991;269:406–68.
- [4] Oleinik EF, Salamatina OB, Rudnev SN, Shenogin SV. *Polym Sci* 1993;35(11):1532–58.
- [5] Oleinik EF, Shenogin SV, Paramzina TV, Rudnev SN, Shantarovich VP, Azamatova ZK, Pakula T, Fischer EW. *Polym Sci Ser A* 1998;40(12):1187–202.
- [6] Hasan OA, Boyce MC. *Polym Eng Sci* 1995;35:331–44.
- [7] Hasan OA, Boyce MC. *Polymer* 1993;34(24):5085–92.
- [8] Boyce MC, Arruda EM. *Polym Eng Sci* 1990;30(20):1288–98.
- [9] Rose J, Duckett RA, Ward M. *J Mater Sci* 1995;30:5328–34.
- [10] Brüller OS. *Polymer* 1978;19:1195–8.
- [11] Brüller OS. On the time-dependent failure of plastics. In: Williams JG, Pavan A, editors. *Impact and dynamic fracture of polymers and composites*. London: Mechanical Engineering Publications, 1995. p. 281–8 (ESIS 19).
- [12] Castellani L. Private communication.
- [13] Quinson R, Perez J, Rink M, Pavan A. *J Mater Sci* 1996;31:4387–94.
- [14] Lomellini P, Rossi AG. *Makromol Chem* 1990;191:1729–35.
- [15] Oleinik EF. Private communication.