

Attempt to correlate the yield processes above and below the glass transition in glassy polymers

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This paper is concerned with a model which attempts to describe quantitatively, by the same elementary process, the yield behaviour above and below T_g , as well as the effect of annealing on the yield stress. This model links together theories we have previously proposed and relies on the following main assumptions: the deformation processes imply the cooperation of n activated segments and that the free energy increase of an activated segment depends on the structural state of the polymer. A satisfactory agreement is found with yield stress data on polycarbonate (PC), over a very large range of temperatures and strain rates. The correlation between the yield stress and the annealing treatment is also reasonable.

(Keywords: polycarbonate; yield process; free volume; glass transition; annealing; physical ageing)

INTRODUCTION

In a previous paper¹ we proposed a model assuming that, of a change of configuration of n segments of macro- in a change of configuration of n segments of macromolecules activated simultaneously. A segment was defined, as for Robertson's theory², as the smallest chain portion containing two non-rigid and non-colinear bonds. It was considered that the fraction of activated segments could be expressed by the Maxwell-Boltzmann distribution and that the number of activated configurations does not depend on the temperature and the structural state of the polymer.

Later³, it was shown that the entropy related to the yield process was dependent on the structural state and therefore on the thermal history of the sample. This entropy was linked to the WLF relation expressed as a function of a structural temperature θ , which was the chief parameter adopted. This temperature, depending on annealing, was defined as the temperature at which the structure of a sample, in a metastable state, would be in equilibrium. However, the change in configuration of segments was not considered here. The purpose of the present approach is, on the one hand, to link together both preceding models by the formulation of a more complete model giving a much improved description of the yield process, and, on the other hand, to compare it with yield stress data obtained on polycarbonate (PC), over a large range of temperatures above and below T_g , and range of strain rates extending over about 10 decades. Moreover, we intend to apply the same theory to account for the effect of thermal treatments on the yield behaviour.

MODEL

The present approach is aimed at determining the nature

of the yield process and to discern the molecular motions involved. It relies on the following basic assumptions:

(1) The n smallest segments (s.s.) belong to the same macromolecule and constitute a main chain segment between two entanglements (c.s.);

(2) The different activated configurations of a s.s. produce different deformations ε_0 in the direction of an applied stress σ .

From these assumptions we can assume that the deformation of a c.s. is at a maximum when the different ε_0 related to the n s.s. it contains are also at a maximum (let ε_M equal this deformation). In this case the entropy is at a minimum as only changes of configuration producing the greatest deformations can be taken into account. Let ΔS_m denote this entropy. The vibration mode of a c.s. producing such a deformation is the fundamental mode and therefore, the fraction of c.s. having all their n s.s. activated, is expressed by:

$$\alpha_1 = \left[1 + \exp n \left(-\frac{\Delta S_m}{R} - \frac{\sigma \varepsilon_m V_0 - Q}{RT} \right) \right]^{-1} \quad (1)$$

where V_0 and Q are the volume and the mean increase in energy of a mole of activated s.s. respectively with R and T denoting the gas constant and the absolute temperature. The smallest deformation ε_m and the highest entropy S_M are linked to the highest frequency mode; in this case the n s.s. is given by:

$$\alpha_1 = \left[1 + \exp \left(-\frac{\Delta S_M}{R} - \frac{\sigma \varepsilon_m V_0 - Q}{RT} \right) \right]^{-n} \quad (2)$$

For a first approximation, we will not consider other modes. According to these hypotheses, the strain rate to yield may be written:

$$\dot{\epsilon} = \nu_m \epsilon_M \alpha_1 + \nu_M \epsilon_m \alpha_2 \quad (3)$$

where ν_m and ν_M are the vibration frequencies of both modes respectively related to c.s. and s.s.

Activated states imply flexed bonds and because a bond can be flexed in two orientations, one of which produces a higher deformation in the direction of the stress, we will assume that:

$$\exp\left(\frac{\Delta S_M}{R}\right) = 2 \exp\left(\frac{\Delta S_m}{R}\right) \quad (4)$$

We will take a single vibration frequency defined by:

$$\nu_0 = \nu_m \epsilon_M = \nu_M \epsilon_m \quad (5)$$

Such an approximation allows us to reduce the number of adjustable parameters and is justified if one considers that both ν_m and ν_M must be close to the Debye frequency and that $\nu_M > \nu_m$ and $\epsilon_M > \epsilon_m$.

From equations (1), (2), (4) and (5), relation (3) becomes:

$$\dot{\epsilon} = \nu_0 \left[1 + \exp n \left(-\frac{\Delta S_m}{R} - \frac{\sigma \epsilon_m V_0 - Q}{RT} \right) \right]^{-1} + \left[1 + 2 \exp \left(-\frac{\Delta S_m}{R} - \frac{\sigma \epsilon_m V_0 - Q}{RT} \right) \right]^{-n} \quad (6)$$

giving the general relation between strain rate, tensile yield stress and temperature.

The first term refers to α_1 , the second to α_2 and the form of the equation makes it easier to consider differing and particular cases. For high stresses and low temperatures $\alpha_1 \gg \alpha_2$, while, on the contrary, $\alpha_1 \ll \alpha_2$ at low stresses and high temperatures. We shall now analyse these cases and the related ranges of experimental conditions suited to them.

Yield behaviour below T_g under high stresses

In this range, it may be considered that equation (6) reduces to:

$$\dot{\epsilon} \simeq \nu_0 \exp \frac{n \Delta S_m}{R} \exp \left(\frac{n \sigma \epsilon_m V_0 - n Q}{RT} \right) \quad (7)$$

This relation has to be compared with the equation for the yield behaviour below T_g given previously³ as:

$$\dot{\epsilon} = \frac{1}{2C(\theta)} \exp \left(\frac{\sigma}{AT} - \frac{Q_0}{RT} \right) \quad (8)$$

with

$$\log C(\theta) = \log C - \frac{c_1(\theta - T_g)}{c_2 + (\theta - T_g)} \quad (9)$$

where Q_0 denotes the activation energy of the yield process, A and C are constants and c_1 and c_2 are the WLF parameters.

Relation (9) may be rewritten as:

$$\ln C(\theta) = \ln C_0 + \frac{2.303c_1c_2}{\theta - \theta_0} \quad (10)$$

with $\theta_0 = T_g - c_2$ and C_0 is constant.

Therefore, it follows from relations (7), (8) and (10) that:

$$n \epsilon_M V_0 = R/A \quad (11)$$

$$nQ = Q_0 \quad (12)$$

and

$$\ln 2C_0 + \frac{2.303c_1c_2}{\theta - \theta_0} = -\ln \nu_0 - \frac{n \Delta S_m}{R} \quad (13)$$

This last equation allows us to define the following constants expressed from the WLF equation, the physical meaning of which has been much discussed in the literature:

$$\Delta S_0 = \Delta S_m + \frac{R\theta_1}{\theta - \theta_0} = -\frac{R}{n} \ln 2C_0 \nu_0 \quad (14)$$

$$n\theta_1 = 2.303c_1c_2 \quad (15)$$

According to equations (13), (14) and (15), $\log C_0$ may now be written as a function of the constant term of the entropy ΔS_0 and the frequency factor ν_0 , however, we should point out that from this form, both constants cannot be separated experimentally.

Yield behaviour above T_g under small stresses

In this range, taking into account equation (14), equation (6) reduces to:

$$\dot{\epsilon} \simeq \nu_0 \left[1 + \frac{1}{2} \exp \left(-\frac{\Delta S_0}{R} + \frac{\theta_1}{\theta - \theta_0} - \frac{\sigma \epsilon_m V_0 - Q}{RT} \right) \right]^n \quad (16)$$

Therefore, it becomes necessary, to measure the values of ν_0 and ΔS_0 separately in order to calculate the strain rate.

Annealing process

It has been assumed in a previous paper³, that, both the yield process and the structural change occurring during annealing may be expressed using equations characterized by the same free energy. Moreover, in the present treatment, we postulate that both processes are identical, implying that annealing comprises of configurational changes occurring at zero stress. The frequency of such events is given by:

$$J = \nu_1 \alpha_2 \quad (17)$$

where ν_1 is a frequency factor probably higher than ν_0 because it must contain an entropy term accounting for changes of configuration not considered in equation (2), i.e. those that would imply negative or insignificant work of the stress during the yield process. Then, applying the same relation as previously³, it follows that

$$d\theta = -(\theta - T_A)J dt \quad (18)$$

where T_A is the annealing temperature and t is the annealing time. Therefore we are able to calculate θ as a function of t and finally, using equation (5), the yield stress of aged samples.

EXPERIMENTAL

We intended to check the validity of the proposed model using tensile tests performed, on one hand, below and above T_g within a range of strain rates as wide as possible; and, on the other hand, at room temperature and constant strain rate, on samples annealed for various times at temperatures near, but below, T_g .

Samples

Makrolon (Bayer) with a viscosity average molecular

weight of 26 000 was used throughout. Tensile test-pieces were machined from the same 0.2 cm thick extruded sheet.

Tensile tests at various temperatures and strain rates

Tensile tests were carried out inside environmental chambers using:

- (i) An Instron tensile machine within the following range of strain rates expressed in s^{-1} : $-5 < \log \dot{\epsilon} < +0.7$.
- (ii) A hydropneumatic high speed tensile machine made in our laboratory, for: $-1.5 < \log \dot{\epsilon} < +2$.
- (iii) Creep equipment for: $-7.7 < \log \dot{\epsilon} < -4$.

Ranges of strain rates related to the different testing machines overlapped, allowing us to check that the data obtained with the different equipments agree to within experimental errors.

Specimens tested below T_g required a thermal pre-treatment in order to ensure a constant structural state (48 h at 406 K). Therefore, an involuntary thermal treatment inside the environmental chamber was avoided for tests performed below and at 406 K.

Prior to being tested near or above T_g , specimens had to remain at the temperature of the test for sufficient time to be at equilibrium (4h at 416 K and 1h at temperatures higher than 416 K).

Tensile tests on annealed specimens

Experimental details about these measurements have been given elsewhere³.

Yield stresses

All the considered tensile curves exhibited a well defined upper yield point at which the deformation and the strain rate were still homogeneous. During the yield drop, necking was observed for tensile tests performed below T_g , but no necking occurred in the vicinity of and above T_g . The engineering upper yield stresses denoted by σ_y , were used throughout. For creep tests, the yield conditions were determined using a previously described method⁴.

RESULTS

In *Figure 1* the ratio of the yield stress to temperature as a function of the logarithm of strain rate is plotted. Isotherms have been drawn through the data, representing the response of the model. *Figure 2* gives a plot of

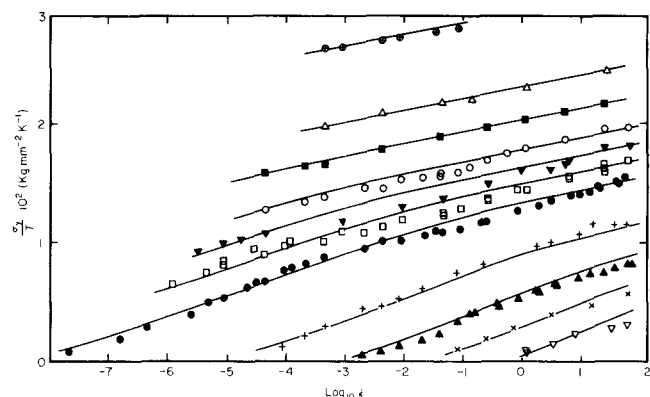


Figure 1 Ratio of the engineering yield stress to temperature against the logarithm of the strain rate ($\dot{\epsilon}$ in s^{-1}). Curves are calculated from equation (6) and *Table 1*. Temperature T of the tests, the structural temperature θ and the key symbols are given in *Table 2*

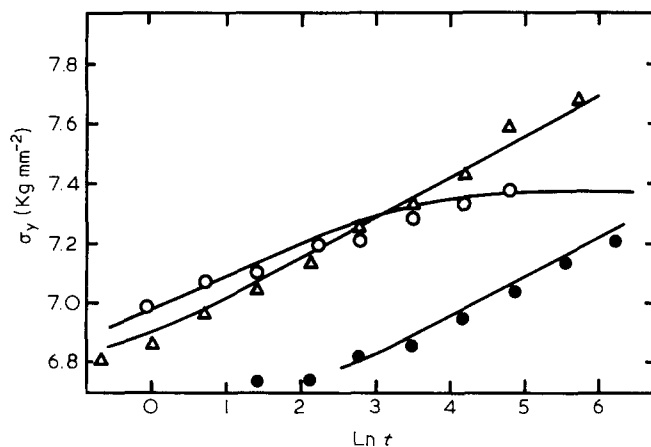


Figure 2 Yield stress at 22°C and constant strain rate $\dot{\epsilon} = 4.17 \cdot 10^{-1} s^{-1}$ as a function of the logarithm of the annealing time (in hours). Annealing treatments are performed at the following temperatures: 110°C (●), 130°C (△) and 140°C (○). Curves are calculated from equations (6) and (18) using the values of the parameters listed in *Table 1*

the yield stress, measured at constant strain rate and room temperature, as a function of the annealing time of the samples at three different temperatures. Again, full lines are theoretical.

The value of the nine parameters allowing the model to fit to the experimental data are listed in *Table 1*. Six of these were imposed:

- (1) The value of n was taken from the results of Donald and Kramer⁵. They found that the molecular weight M_c of a c.s. of PC reaches $2490 g mol^{-1}$; i.e. about 20 pairs of flexible and non-colinear bonds (this number is close to $n=25$ previously estimated for PVC and PMMA¹).
- (2) θ_0 and θ_1 were calculated using relations (10) and (15) taking $c_1 = 17.4$, $c_2 = 50$ and $T_g = 147^\circ C$ which are practically the universal values of the WLF constants and the glass transition temperature of PC.
- (3) At low temperatures, where a constant structural state may be assumed, relation (8), derived from the Eyring theory accurately fits the experimental data. The three parameters implied, namely A , Q_0 and $C(\theta)$ which were evaluated in a previous paper³, allows us to calculate Q , $R/\epsilon_m V_0$ and $(n/R)\Delta S_0 + \ln v_0$ using respectively relations (11), (12) and:

$$(n/R)\Delta S_0 + \ln v_0 = \ln 2C(\theta) - \frac{2.303c_1c_2}{c_2 + (\theta - T_g)} \quad (19)$$

combining equations (10), (13) and (14).

The three remaining parameters were adjusted as follows:

The slope of the curve related to 416K given in *Figure 1*, allows us to calculate $R/\epsilon_m V_0$ while the horizontal position of this curve is used to separate $\Delta S_0/R$ and $\ln v_0$ in relation (19).

Finally, v_1 was evaluated by adjusting the horizontal position of the curve obtained at 403K given in *Figure 2*.

The agreement between theory and data is satisfactory, particularly if we consider the large range of temperatures and strain rates investigated. Nevertheless, an inspection of *Figure 1* shows that, within the transition range between the α_1 and α_2 processes, yield stress data are

Table 1 Values of the constants used in equation (6) to generate the curves in *Figures 1 and 2*

n	Q (cal mol ⁻¹)	θ_0 (K)	θ_1 (K)	$\log \nu_0$ (s ⁻¹)	$\log \nu_1$ (s ⁻¹)	$R/\varepsilon_m V_0$ (kg mm ⁻² K ⁻¹)	$R/\varepsilon_m V_0 n$ (kg mm ⁻² K ⁻¹)	$\varepsilon S_0/R$
20	3800	370	100	11.4	12.5	$4.35 \cdot 10^{-4}$	$6.15 \cdot 10^{-4}$	75

Table 2 Temperature T , structural temperature θ and key symbols related to *Figure 1*

Key symbols	⊕	△	■	○	▼	□	●	+	▲	X	▽
T (K)	295	323	353	373	386	396	406	416	421	426	431
θ (K)	408.5	408.5	408.5	408.5	408.5	409	410	416	421	426	431

slightly lower than that predicted by the model. This may be due to the fact that we have only considered two limiting modes of deformation, neglecting the others.

DISCUSSION

The optimum agreement between theory and data requires us to choose at 396K and 406K a structural temperature θ , slightly higher than the value used at lower temperatures. This agrees with the results of Kovacs *et al.*⁶ concerning indirect quenching of polymers (samples are first quenched at a temperature below the further isothermal treatment). Indeed, they measured a dilatation of the samples preceding a constant contraction and concluded that elements having short relaxation times can equilibrate their free volume with the thermal bath even below T_g . This volume increase must parallel an increase in θ .

Mercier and Groeninckx⁷, in isothermal relaxation tests on PC, measured a shift factor which fits the WLF equation with the universal values of c_1 and c_2 . It is also worth pointing out, that in the range between T_g and $T_g + 100^\circ\text{C}$, where the shift factor extends over 11.5 decades, differences between the values of this quantity, calculated respectively from the WLF equation and from equation (6), are smaller than 0.2 decades, i.e. within experimental accuracy. Moreover, this agrees with yield stress results on PC and PVC⁸ published previously. Therefore, it seems plausible that stress relaxation above T_g proceeds as a result of the same process as for yielding.

The Debye frequency is close to ν_0 and ν_1 ; ν_1 is found to be slightly higher than ν_0 as we presumed; moreover ν_0 is close to the frequency factor of the β process⁹. Does this mean that the β process does not contain an entropy factor and, for this reason, is not affected by annealing¹⁰? Legrand's data¹¹ related to isothermal densification of PC during annealing gave, in any case, contractions lower than 10^{-3} . Using the following equation:

$$\frac{\Delta V}{V} = \Delta\alpha \cdot \Delta\theta \quad (20)$$

where V is the specific volume and $\Delta\alpha$ the difference between thermal expansions above and below T_g , we obtain values of $\Delta\theta$ about four times lower than those required to fit equation (18) to the data. However, the enthalpy relaxation measurements³ agree with equation (18). Therefore, it could be suggested that free volume is probably not the main physical quantity which defines the structural temperature. We intend to come back to this subject in a future paper.

CONCLUSIONS

The fit between the response of the present model and experimental yield stress data, reinforces our point of view and basic assumption that the same elementary process is involved at yield above and below T_g as well as during annealing. This process consists of a change of configuration implying the activation of the smallest segments containing two flexible and non-colinear bonds.

The main conclusion is that our treatment reduces to an Eyring-type equation below T_g and to a WLF-type equation above T_g respectively. Nevertheless, the meaning of the structural temperature is not yet clear, nor the nature of the corresponding entropy.

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