Effect of thermal history on the tensile yield stress of polycarbonate in the β transition range

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The tensile yield behaviour of three forms of polycarbonate differing in their thermal history is investigated, at constant strain rate, over a wide range of temperatures (–140° to +80°C). The plot of the yield stress *versus* temperature exhibits a thermal history dependence over the whole range explored and reveals the β transition which is located at the same temperature T_β for the three forms. The yield behaviour is described assuming that two activated processes α and β requiring additive stresses are involved. The β component of the yield stress is found to be insensitive to thermal history as well as the related loss peak. Only the α process is affected; details concerning this dependence are discussed.

Keywords Polycarbonate; β transition; thermal history; physical ageing; yield stress; rate process

INTRODUCTION

For several years, we have proposed to describe the yield behaviour of glassy polymers by (at least) two Eyring processes operating in parallel[1-6], namely the α and β activated processes. This point of view is supported by other authors: Roetling[7-9], Gonze and Chauffoureaux[10] and more recently by Ward *et al.*[11,12]

In the case of poly(vinyl chloride) (PVC), polycarbonate (PC) and poly(methyl methacrylate) (PMMA), the β yield process has been correlated with the β shear relaxation peak[3,5,6,10]. The purpose of this paper is to come back to this subject by investigating the yield behaviour, over a wide range of temperatures, of three forms of PC differing in their thermal histories (original, quenched and annealed below the glass transition temperature T_g).

It is checked that these thermal histories do not affect the intensity of the β shear loss peak, nor its position on the temperature axis; this result is similar to those of Allen *et al.*[13] and Struik[14].

According to our proposed model, this fact implies that the β process contribution to the yield stress is insensitive to quenching or annealing.

Since the early work of Golden *et al.*[15], it is well known that thermal pretreatments increase the yield stress of glassy polymers, measured at room temperature, but the effect on the yield behaviour at low temperatures was still ignored.

We intend to show that, throughout the range explored, the α process contribution to the yield stress does indeed depend on thermal history and to confirm the previous statement[16,17] that this dependence appears solely through the parameter containing the frequency factor of the related molecular movement (i.e. the parameters associated with the activation energy or the rheological volume remain nearly unchanged).

EXPERIMENTAL

Material

Makrolon (Bayer) was used throughout. It has a viscosity average molecular weight of 26 000 which is not affected by quenching or annealing treatments.

The initial untreated state is the 'as-received' one, and it is called 'original'.

Thermal pretreatments

Specimens of original PC are converted into the annealed form by heating for 2 h at 130°C and air cooling, and into the quenched form by annealing for 1 h at 160°C and ice quenching.

The annealing conditions below the glass transition ($T_g \simeq 145$°C) are chosen to give an appreciable increase of the tensile yield stress measured at room temperature[17]. The treatment was performed inside a dry oven. Quenched specimens were tested 6 days later, considering that after such a time transient effects have vanished.

Specimens

Tensile and damping test-pieces are machined from the same extruded sheet 0.2 cm thick. The shape of the tensile test-pieces is given elsewhere[2]. In order to prevent rupture before yielding at low temperatures, the machined surfaces were carefully polished with several grades of emery paper. Annealed specimens are more brittle than the others. Before being tested below −100°C, they are smoothly reduced in width around the middle in order to avoid rupture from the fillet below the yield point.

Measurements

The damping tests were carried out using a free oscillation pendulum at frequencies of about 1 Hz from −155° to 0°C.

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Experimental details have been given previously[16].

The equipment used in tensile tests in order to determine the yield stress is described elsewhere[2]. Tests were performed at a strain rate equal to $4.16 \times 10^{-4} s^{-1}$ from about $-140°$ to $+80°C$.

Engineering stresses are considered.

We avoided the range of temperatures where an involuntary thermal treatment may take place during the test; this is the reason why 80°C is the highest temperature explored[13].

RESULTS

Damping tests

In *Figure 1*, the $\tan\delta$ loss curve is given for the three forms of PC; no difference can be discerned in the position or the maximum value of the peak. Only the shape of the high temperature side differs slightly; so that we consider that the shear loss peak located at $-100°C$ for 1 Hz is not affected by thermal history.

We call this peak the β peak of PC, using Sauer's system of nomenclature[18]. In our view, the related molecular motion is also revealed by a break in the curve, giving the yield stress as a function of temperature at constant strain rate (see *Figure 2*).

Previously[16,19], we have explored in damping tests the range between $-80°$ and $+140°C$ and recognized the existence of an intermediate peak between the β and the glass temperature or α peak, in the original and quenched forms. This intermediate peak, which disappears on annealing, is not revealed as a break in the yield stress *versus* temperature curve although we think it affects the value of the yield stress.

We look on this peak as belonging to the low-temperature tail of the glass transition peak; the exhibited maximum is perhaps nothing else than an artifact as advanced previously. Although this peak does not exist for all the forms of PC, it is sometimes called the β peak of PC in the literature; in this case the loss peak at $-100°C$ and 1 Hz is denoted by γ.

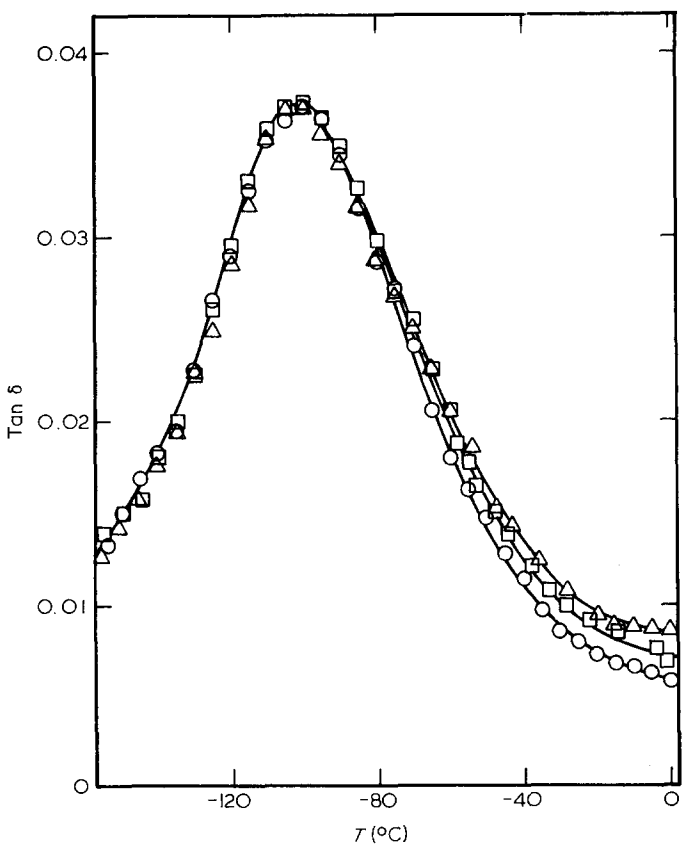

Figure 1 Shear loss curve at about 1 Hz for the three different forms of PC (○, □ and △ refer to the original, quenched and annealed PC respectively)

Tensile tests

In *Figure 2*, we have plotted the tensile yield stress *versus* temperature, at constant strain rate, for the three considered PC forms. Throughout the data, it is possible to draw, for each form, two asymptotic directions intersecting at the same temperature $T_\beta = -70°C$. This temperature is chosen to characterize the obvious break on the curves. Only one asymptotic direction is given on the graph, for clarity.

The original form is cooled more slowly through T_g than the quenched form, which produces similar mechanical effects to annealing below T_g. At constant temperature and strain rate, over all the explored range, we find from *Figure 2* that the following relation holds:

$$\sigma_a > \sigma_o > \sigma_q \tag{1}$$

where subscripts o, q and a are related to the three different forms respectively. From this Figure, it can be seen that the data tend to merge at low temperatures, but this fact can be explained precisely by the structure of the Eyring equation that we use to express the yield stress. In the temperature range from $-70°$ to $+80°C$ (i.e. the α range), it may be considered that only the α process requires a stress contribution at yield, σ_α, which can be expressed by the exponential form of the Eyring equation:

$$\sigma_\alpha = A_\alpha \left(T \ln(2C_\alpha \dot{\varepsilon}) + \frac{Q_\alpha}{R} \right) \tag{2}$$

with constant values of A_α, C_α and Q_α; R denoting the universal gas constant and $\dot{\varepsilon}$ the strain rate. The parameters A_α, Q_α and C_α have been developed by one of us as a function of the segmental motion leading to yield deformation[20].

Our previous results[16,17] allow us to assume that only C_α, which is related to the frequency factor of the α process, is appreciably affected by thermal history, while the activation energy Q_α is hardly influenced and A_α, which contains the activation volume, remains the same.

The change in C_α brought about by a thermal pretreatment has been expressed previously[17], and derives from a change of configurational entropy.

Let us consider that only C_α differs from one form to the other. It follows, taking into account (2), that the value of σ_α extrapolated to zero kelvin (0 K) does not depend on thermal history. In fact, it is possible to draw throughout the data three asymptotes related to the α range, intersecting at zero kelvin (shown in *Figure 2*). The straight lines given on this Figure are calculated from (2) with the value of the constants given in *Table 1*.

Below T_β, it follows from the proposed model that the measured yield stress includes two additive components:

$$\sigma = \sigma_\alpha + \sigma_\beta \tag{3}$$

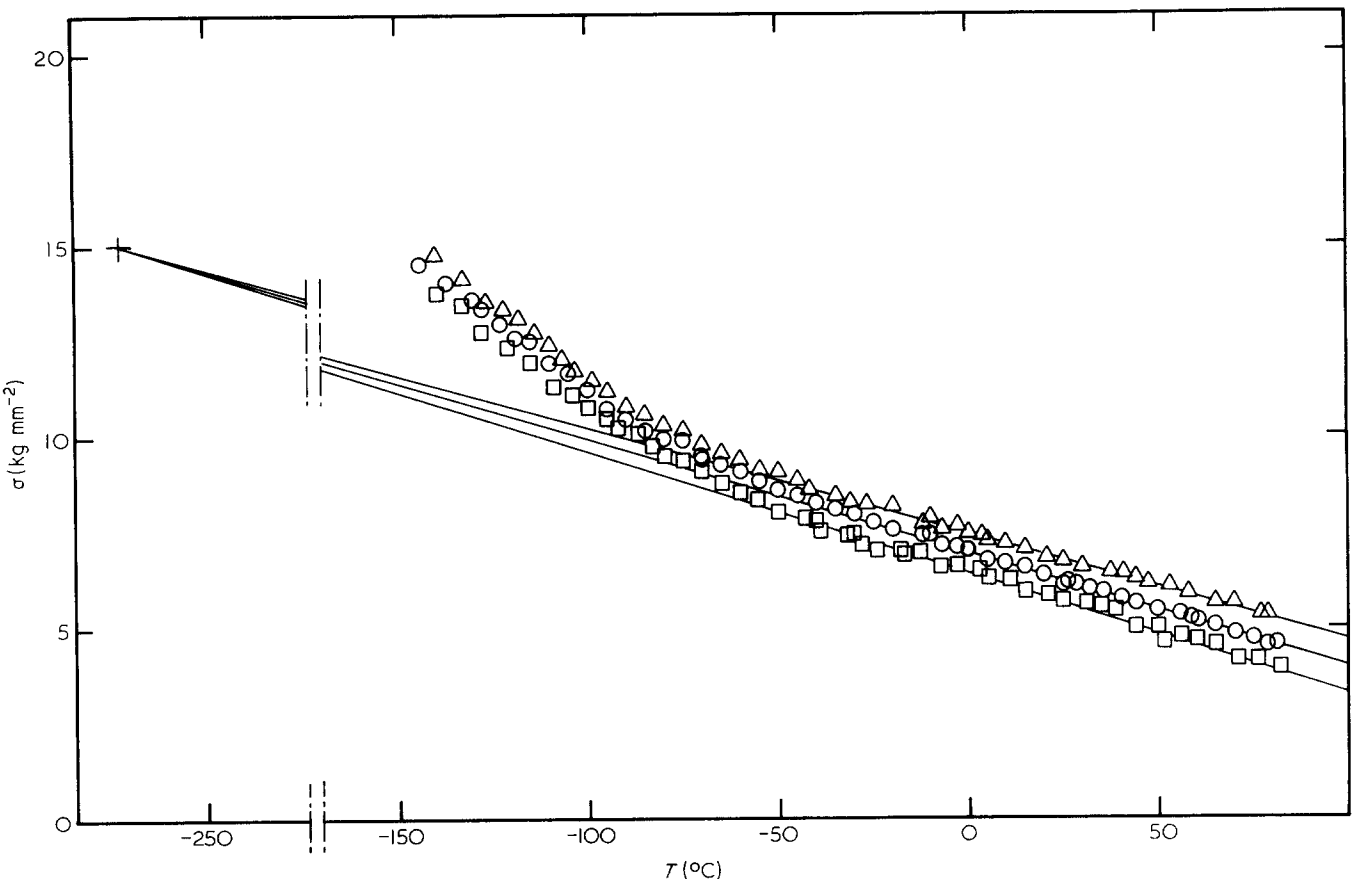

Figure 2 Plot of the tensile yield stress *versus* temperature at constant strain rate (○, □ and △ refer to the original, quenched and annealed forms respectively). Straight lines fit equation (2) with the constants given in *Table 1*

Table 1 Values of the constants of equation (2)

A_α (kg mm^{-2} K^{-1})	Q_α (kcal mol^{-1})	C_α (s)	
4×10^{-4}	75	original:	7.23×10^{-30}
		quenched:	8.09×10^{-32}
		annealed:	5.86×10^{-28}

The asymptotic value of σ_β is expressed in the same manner as σ_α by:

$$\sigma_\beta = A_\beta\left(T \ln(2C_\beta\dot{\varepsilon}) + \frac{Q_\beta}{R}\right) \quad (4)$$

In this case, we will assume that C_β as well as A_β and Q_β do not depend on thermal history, which is supported by the fact that the β peak, and therefore the β process, is not affected. If so, in this range also, different thermal histories are revealed by straight lines intersecting at zero kelvin, in a plot of σ *versus* temperature.

The graph of *Figure 3* shows perhaps more clearly that the β process is not affected by thermal history. There we have plotted, for the three forms, σ_β as a function of temperature. The data were obtained by subtracting from the measured yield stress, the extrapolated value of σ_α, calculated from equation (2). Below T_β, a single asymptote may be drawn throughout the data related to the three considered PC forms.

DETERMINATION OF THE PARAMETERS

The α process

The value of the parameters of equation (2), given in *Table 1*, are obtained as follows. First A_α is measured at constant temperature (28°C) belonging to the α range, in a plot of σ/T *versus* ln $\dot{\varepsilon}$ ($\dot{\varepsilon}$ varied from 4.17×10^{-5} to 8.3×10^{-2} s^{-1}) by means of a least-squares linear regression. Data are related to the original form. The plot of *Figure 2* is used to find the bundle of straight lines which best agree with the data and intersect at zero kelvin. A common value of $A_\alpha Q_\alpha/R$ is then obtained as the intercept. From the same graph C_α is determined for each form by extrapolating to zero stress.

Table 2 Values of the constants of equation (4)

A_β (kg mm^{-2} K^{-1})	Q_β (kcal mol^{-1})	C_β (s)
1.85×10^{-3}	9.6	5.74×10^{-8}

The β process

The determination of A_β is not so easy and accurate as A_α; at low temperatures it is not possible to explore a large range of strain rates in order to obtain the yield stress because glassy polymers become brittle at high strain rates.

Values of C_β and $A_\beta Q_\beta/R$ may be rather accurately obtained using the graph of *Figure 3* and extrapolating the asymptotic direction related to σ_β to zero kelvin and to zero stress. An estimate of A_β may be obtained from $A_\beta Q_\beta/R$ and the value of Q_β previously found[5] (see *Table 2*).

CONCLUSIONS

Assuming that two activated processes α and β, operating in parallel, are required to explain the yield behaviour of

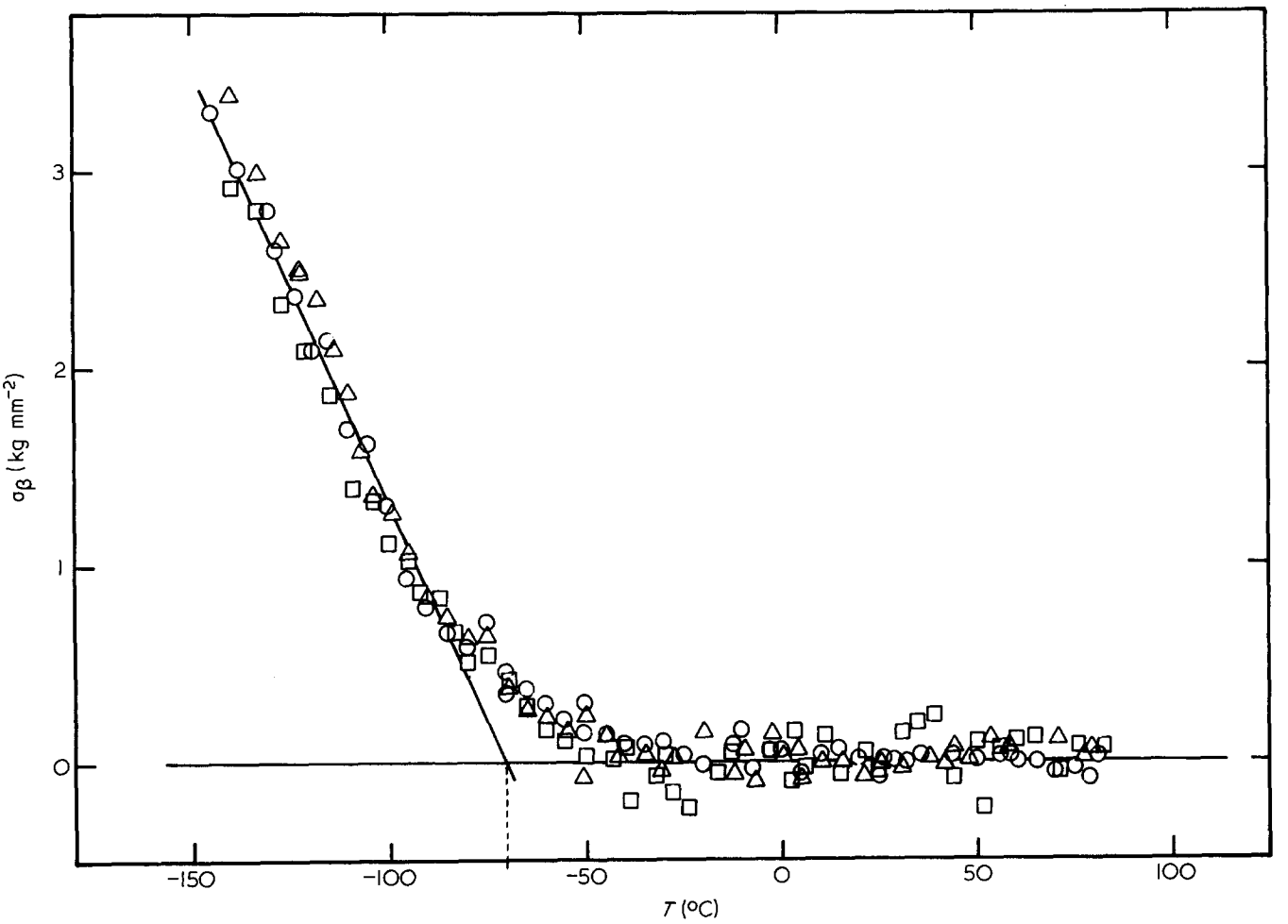

Figure 3 A plot of the β component of the yield stress *versus* temperature at constant strain rate (○, □ and △ refer to the original, quenched and annealed forms respectively)

PC at low temperatures, the present investigation shows that:

(i) the β contribution to the tensile yield stress is unaffected by changes in thermal history; and

(ii) the α contribution is influenced over all the range explored.

Using the Eyring formalism to express the α and β components of the yield stress, our results confirm that only one parameter reflects appreciably the effect of thermal history. This parameter is related to the entropy factor of the molecular motion corresponding to the α process.

The present contribution is partially in contradiction with the work of Struik on physical ageing in amorphous polymers. Although we agree completely with this author when he notices that the β shear peak of PC and secondary relaxation processes are unaffected by changes in thermal history, we disagree when he claims that the ageing effect disappears at low temperatures, i.e. the ageing range is bounded by T_β as the lower bound[14]. The last conclusion was drawn from damping measurements which reflect only a partial aspect of the problem.

Obviously, the results proposed here are based on the assumption that two processes requiring additive stresses are involved at yield. This implies that the temperature T_β cannot be viewed as a critical temperature separating two ranges, each characterized by its own mechanism of yield deformation, as advanced by Escaig *et al.*[21,22] It is simply the temperature above which the β process contribution to the yield stress vanishes at constant strain rate.

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