Effect of annealing on the shear yield stress of rejuvenated polycarbonate

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The effect of annealing below T_g on rejuvenated samples of polycarbonate has been investigated through torsional yield stress measurements. Rejuvenation was achieved by twisting thin-walled tubular specimens at constant rotation rate well beyond the yield point. The direction of twisting was reversed twice in order to obtain an hysteretic curve. Rejuvenated samples were then annealed and retested in torsion. The ratio of the shear yield stresses after and before the annealing treatment is followed as a function of the annealing conditions. Numerous data are obtained here allowing an accurate check of the response of a model previously proposed relying on the Eyring formalism and the Davies–Jones equation rewritten as a function of θ, the structural temperature of the sample.

(Keywords: polycarbonate; annealing; rejuvenation; structural temperature; torsion test)

INTRODUCTION

For the past few years we have been investigating the effect of annealing pretreatments at temperatures below T_g, on the tensile yield stress and enthalpy relaxation of samples of polycarbonate (PC) having different thermal and mechanical histories[1–3]. It was proposed to find the relationship between the evolution of these properties upon annealing and the structural state of the sample. We took as the main factor to be considered in annealing investigations, the structural temperature θ, i.e. the temperature at which the structural state of the sample associated to a given treatment would be in equilibrium. Annealing was found to decrease the θ value of the sample, while quenching from above T_g or plastic deformation increases this value. The latter treatments are known to produce rejuvenation effects; those related to plastic deformation appeared to be stronger (at least in the case of PC).

The θ dependence of the tensile yield stress was established experimentally from samples annealed in the range $T_g - 10\,\mathrm{K}$ to T_g, where it may be considered that θ reaches the annealing temperature. Our measurements led us to state that a decrease of 3 K in θ has the same effect on the tensile yield stress as an increase of the strain rate by a factor of ten[2]. In order to look more closely into the effect of θ changes on the PC yield, we turned towards the annealing effect or rejuvenated samples which allows investigation of a larger range of θ values. Recently[3], we have calculated θ as a function of the annealing conditions: temperature T_a and time t_a. These theoretical results were adjusted to account for enthalpy relaxation measurements related to quenched and mechanically rejuvenated PC samples annealed in various conditions. Using the same model, we intend now to account for the effect of annealing on the shear yield stress of rejuvenated PC samples.

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EXPERIMENTAL

Method

We have chosen to rejuvenate the material by plastic deformation in torsion of thin-walled samples. In such a mode of deformation, no neck occurs and the shape of the sample remains nearly the same throughout the test[4]. Samples were twisted in torsion well beyond the yield point, the direction of twisting was then reversed twice in order to obtain a cyclic curve. Next the samples were annealed and recycled in torsion. Examples of pairs of stress–strain curves are given in *Figure 1*; the offset between the curves for the first and second cycles is arbitrary. From these two torsional cycles, on the same sample, the ratio τ_θ/τ_i was obtained where τ_i and τ_θ denote the yield stress related to the 'as received' and the annealed rejuvenated state of the sample, respectively. This reduced expression of the shear yield stress is convenient for two reasons: first, it can be obtained from the related torques, so errors due to machining and cross-section measurements are avoided; second, it leads to a theoretical expression derived from the Eyring equation which contains no adjustable parameter, provided the difference $\theta - \theta_i$ in the structural temperatures of the sample is known.

Samples

Samples were machined from rods of commercial grade Lexan PC in order to obtain thin-walled tubes with flat ends, the shape and dimensions of which are given in *Figure 2*. The ratio of the mean radius of the tube to the wall thickness is 8.5, a value large enough to consider that the stress is uniform throughout the wall of the tube. Most of the data were obtained on samples in the initial 'as received' state related to θ_i; but some samples were pre-annealed 46 h at 120°C before being tested in torsion in

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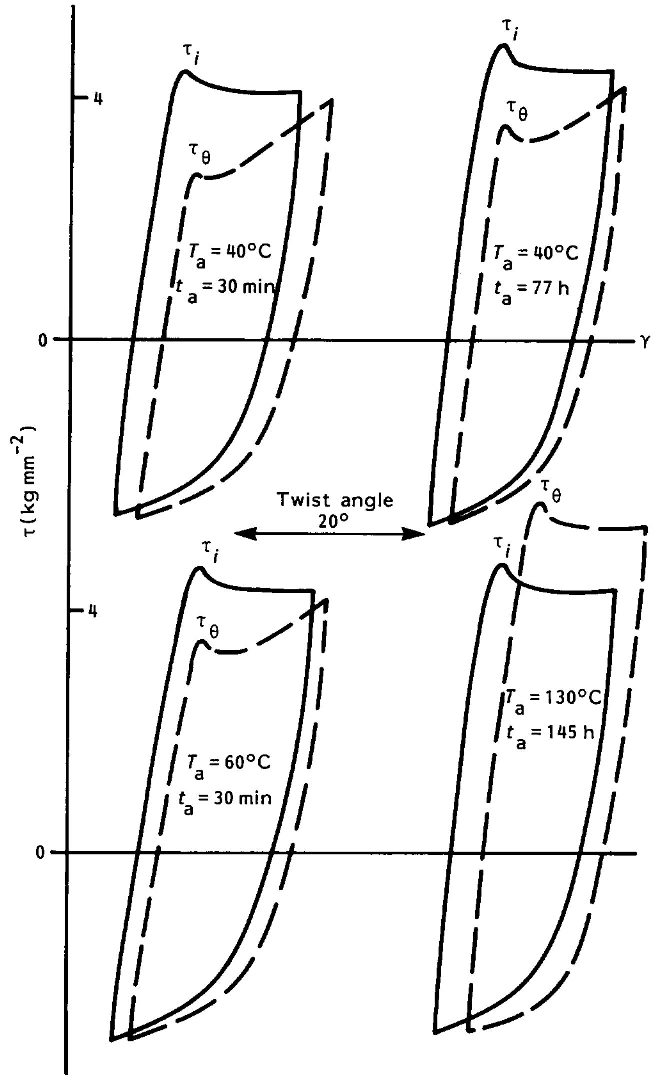

Figure 1 Examples of pairs of torsional stress–strain curves. Each pair is related to the same sample. Annealing was performed after the first cycle. ———, First cycle; – – –, second cycle

order to give them a different θ_i value. Thermal treatments were performed inside a dry oven.

Torsion tests

The testing machine consisted of a rigid support and a rotating shaft. The axis of the shaft was carefully aligned with the specimen grips so that a pure axial twist was applied to the sample. Upon twisting, the torque in the sample and the angle of twist were measured by a strain gauge load cell and from the rotating shaft, respectively. Torque and twist were recorded. All tests were performed at room temperature at constant rotation rate giving a strain-rate $\dot{\gamma} = 2.47 \times 10^{-2}\,s^{-1}$. All the samples were deformed by twisting to the same strain $\gamma = 0.74$, i.e. an angle of 20°. The direction of twist was reversed until the extrapolation of the initial tangent of the curve was met and then reversed a second time in order to obtain a cyclic curve. At the end of the test, it may be considered that torque and strain reached zero, and that the sample has then recovered its original shape and dimensions. Let us point out that when the curve closes perfectly, a recovery force of about 8% of the yield strength appears instantaneously and remains quasi constant as long as the sample stays in the test machine. It corresponds to an angle of twist of 1° and is of the order of the force appearing at the beginning of the test when the flat ends of the sample are not absolutely parallel. Such errors, inherent in the method, are not significant and do not seem to increase data scatter.

DATA ANALYSIS

Rejuvenation effect

The yield stress of samples re-tested at room temperature immediately after the first cycle was reduced by half, indicating a significant rejuvenation effect due to plastic deformation (*Figure 3a*). It is worthwhile noticing that for samples twisted only up to the yield point during the first cycle and re-tested immediately at room temperature, the yield stress remains unchanged and no rejuvenation effect occurs (*Figure 3b*).

Yield behaviour of annealed rejuvenated samples

We investigated the ratio τ_θ/τ_i as a function of t_a from 40°C to very near T_g; all the stress–strain curves exhibit a defined yield point. Data are given in *Figure 4* where, at

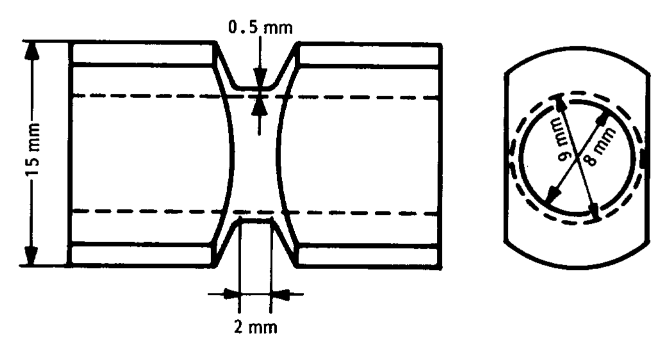

Figure 2 Shape and dimensions of the specimen for torsion tests

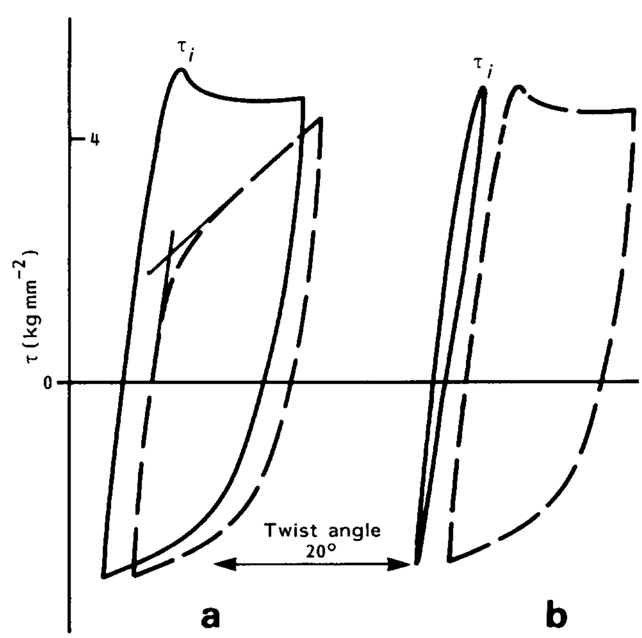

Figure 3 Pairs of torsional stress–strain curves for samples re-tested immediately after the first cycle. a: Sample twisted well beyond the yield point and therefore rejuvenated; b: sample twisted only up to the yield point. ———, First cycle; – – –, second cycle

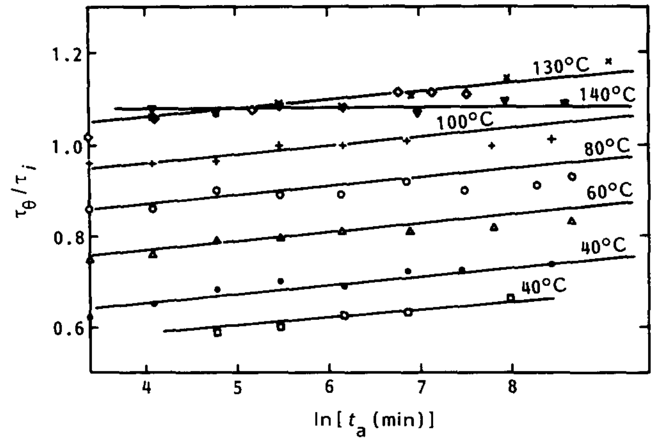

Figure 4 Plot of the torsional ratio as a function of ln t_a at a series of constant T_a related to annealed rejuvenated samples from the 'as received' initial state (●, △, ○, +, ×, ▽) and from a pre-annealed initial state (□). Data corresponding to annealed but not rejuvenated samples are denoted by ◇. Solid lines are theoretical

constant T_a, a linear dependence between τ_θ/τ_i and ln t_a may be observed. As the checking of our model requires that all the tests are performed at the same testing temperature, shear stresses are then corrected to reduce τ_i or τ_θ to $T=20°C$. Taking into account previous results obtained for tensile yield stresses[5–7], corrections were made by estimating that an increase of 1°C in T lowers the shear yield stress by 0.85%.

In *Figure 5*, the torsional ratio is plotted as a function of T_a for isochronal treatments. Data related to $t_a = 1$ h agree with those obtained by El Bari[8] in similar experiments but with a more sophisticated apparatus allowing simple shear, already used by G'Sell *et al.*[9] Of course, for this comparison data need to be reduced to the same conditions of testing, temperature, strain rate and initial structural state; our model allows such corrections to be made.

Yield behaviour of annealed samples

A few 'as received' samples were submitted to a torsion cycle just at the yield point to determine τ_i, and so were not rejuvenated. After annealing at 130°C, they were re-tested. The ratio τ_θ/τ_i (*Figure 4*) fell amongst the data of annealed rejuvenated samples at 130°C. In this case, the torsional ratio is always greater than unity. For such annealing conditions, the time required to erase the rejuvenation effect is very small compared with t_a.

MODEL

Expression of the torsional ratio

Starting from the Eyring equation, the engineering yield stress, σ, in tensile tests conducted at temperature, T, and strain rate, $\dot{\varepsilon}$, may be expressed by:

$$\sigma/AT = \ln 2\, C(\theta)\dot{\varepsilon} + Q_0/RT \qquad (1)$$

with constant values of A, $C(\theta)$ and Q_0 over a very large range of experimental conditions for samples related to the same θ[1,5–7]. The gas constant is denoted by R.

The only parameter depending on θ was shown to be $C(\theta)$ related to the structural entropy. Let σ_i denote the engineering yield stress of an 'as received' sample and σ_θ that related to a given θ; both stresses refer to tests performed at the same strain rate and temperature. Therefore, from equation (1) the tensile yield stress ratio may be expressed by:

$$\frac{\sigma_\theta}{\sigma_i} = 1 + \frac{AT}{\sigma_i}\ln\frac{C(\theta)}{C(\theta_i)} \qquad (2)$$

As in previous papers, let us take the simple linear relation for the entropy change term, such that:

$$\ln\frac{C(\theta)}{C(\theta_i)} = R^{-1}(\Delta S(\theta_i) - \Delta S(\theta)) = C'(\theta_i - \theta) \qquad (3)$$

where C' is a constant.

Using a yield criterion previously proposed by one of us[10], it can easily be established that:

$$\frac{\tau_\theta}{\tau_i} = \frac{\sigma_\theta}{\sigma_i} \qquad (4)$$

provided torsional and tensile tests are conducted at the same temperature and equivalent strain rate, i.e.

$$\dot{\gamma} = \sqrt{3}\dot{\varepsilon} \qquad (5)$$

Therefore from equations (2)–(4), the torsional ratio may be written:

$$\frac{\tau_\theta}{\tau_i} = 1 - \frac{ATC'}{\sigma_i}(\theta - \theta_i) \qquad (6)$$

Numerical values of the parameters

These values are listed in *Table 1*. The parameter A has been accurately measured in previous papers[1,5]. It

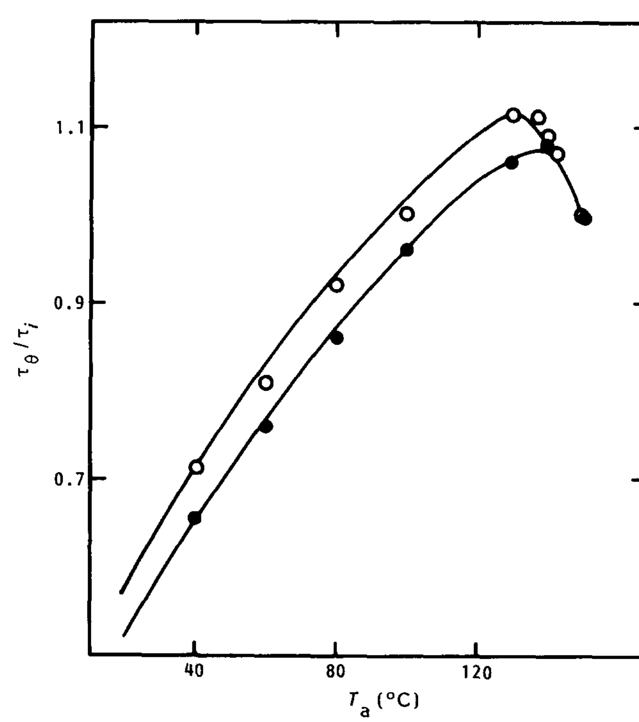

Figure 5 Plot of the torsional ratio as a function of T_a for isochronal annealing on rejuvenated samples. Solid lines are theoretical. ○, $t_a = 16$ h; ●, $t_a = 1$ h

Table 1 Values of the constants used in equation (6) to generate the solid lines in *Figure 4*

Initial state of the sample	A (kg mm^{-2} K^{-1})	T (K)	C' (K^{-1})	σ_i (kg mm^{-2})	θ_i (K)
As received	4.35×10^{-4}	293	0.768	6.98	419.0
Annealed 46 h at 120°C	4.35×10^{-4}	293	0.768	7.69	411.2

characterizes the kinetics of the tensile yield process and may be expressed by:

$$A=[\mathrm{d}\,\sigma/T/\mathrm{d}\ln\dot{\varepsilon}]\ \mathrm{const.}T,\theta \quad (7)$$

It was found not to be affected by thermal or rejuvenation treatments. The parameter C' may also be evaluated by taking into account previous results[2], stating that at constant $\dot{\varepsilon}$ and T, a decrease of 3 K in θ has the same effect on the tensile yield stress as an increase in $\dot{\varepsilon}$ by one decade at constant θ and T. Such experimental results are in agreement with the WLF equation in the T_g temperature range. Therefore from equations (1) and (3), we can write that:

$$C'=(1/3)\,2.303\ \mathrm{K}^{-1} \quad (8)$$

The tensile yield stress σ_i was measured at 20°C and a strain rate equal to $1.43\times10^{-2}\ \mathrm{s}^{-1}$ that checks relation (5). Therefore, from *Table 1* it comes that $(ATC')/\sigma_i=1.4\times10^{-2}\ \mathrm{K}^{-1}$. θ_i was determined from the isotherm $T_a=140$°C on *Figure 4* where τ_θ/τ_i reaches a plateau estimated to equal 1.085 from the mean values of the data. In such a case, it may be assumed that $T_a=\theta$. Therefore θ_i may be evaluated from equation (6) which finally may be rewritten as:

$$\tau_\theta/\tau_i=1-1.4\times10^{-2}(\theta-419) \quad (9)$$

giving the torsional ratio of annealed rejuvenated samples from the 'as received' initial structural state. This ratio may be expressed and evaluated from torsion experiments only. But in that case, an accurate measurement of τ_i is required which cannot be obtained in our tests (only the ratio of the stresses is accurate). Moreover, the kinetics of the torsion yield process must be established over a wide range of shear rates, not available on our testing machine. We therefore preferred to introduce equivalent tensile stresses and use results already published.

θ dependence on the annealing conditions

Let θ_{ir} be the structural temperature of a rejuvenated sample just at the beginning of the thermal treatment. It may be estimated from equation (9) and the torsional ratio of a sample retested immediately after the first cycle (*Figure 2a*); we found 460 K which was taken as the maximum θ value. The variation of θ as a function of t_a at constant T_a was obtained by numerical integration from 460 K of the following differential equation previously derived from the Davies and Jones' equation[11]:

$$\mathrm{d}\theta=\nu(T_a-\theta)\exp\left(C\theta-\frac{Q}{RT_a}\right)\mathrm{d}t_a$$
$$=10^{-96}(T_a-\theta)\exp\left(0.7\theta-\frac{3.2\times10^4}{T_a}\right)\mathrm{d}t_a \quad (10)$$

The numerical values of the parameters C and Q were exactly the same as those adjusted in our last paper[3] using enthalpy relaxation measurements. But a good fit to the present data used $\nu=10^{-96}\ \mathrm{s}^{-1}$ instead of $10^{-95}\ \mathrm{s}^{-1}$. Therefore, we were not able to use exactly the same values for the three parameters as before, as one of them differs slightly. We realized that some kinds of measurements are more sensitive than others to a given parameter. For instance, it makes practically no difference in the fitting of theoretical and experimental enthalpy relaxation results, if a value for ν of 10^{-95} or $10^{-96}\ \mathrm{s}^{-1}$ is used, while it does in the case of the present data. On the other hand, the former results are more sensitive to small changes in the value of Q. *Figure 6* gives the theoretical θ variation throughout a very large range. High θ values refer to annealed rejuvenated samples but since θ reaches θ_i, further decreasing is related to the annealing of samples rejuvenated or not.

COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

The solid lines drawn throughout the data plotted in *Figure 4* are theoretical. They were obtained using equation (9) with the corresponding θ taken from the graph of *Figure 6*; quite good fit may be noticed.

Equation (6) was still used to evaluate the torsional ratio of pre-annealed samples (46 h at 120°C). The related σ_i was measured or equivalently interpolated from tensile

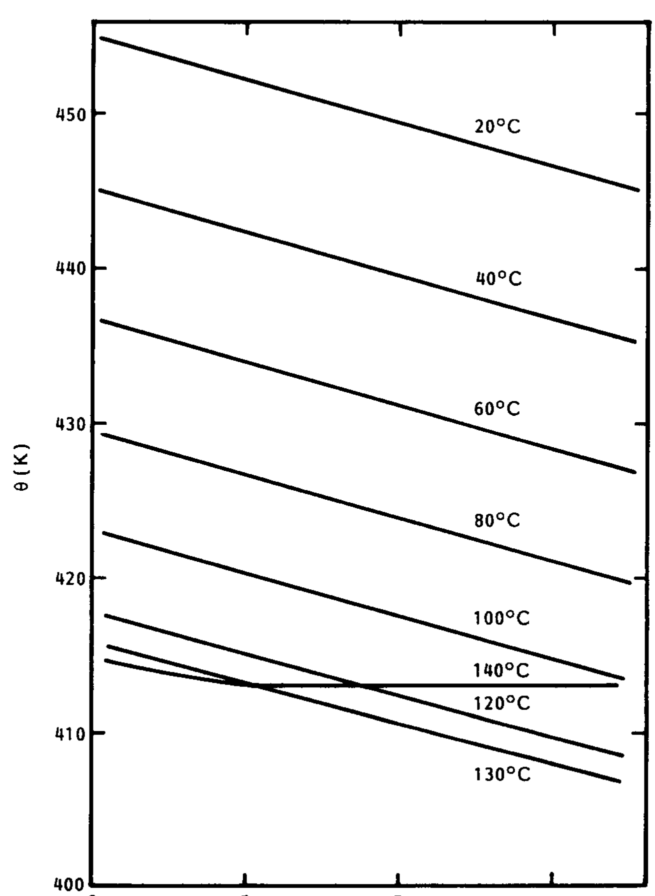

Figure 6 Plot of the calculated θ value as a function of $\ln t_a$ for a series of constant T_a

yield stress data corresponding to the same annealing pretreatment as reported previously[1]. The θ_i value characterizing this treatment was obtained from the graph of *Figure 6*. All the numerical values are given in *Table 1*. Using equation (6) and the θ values relating to the 40°C isotherm of *Figure 6*, a line was drawn on the graph of *Figure 4* which was found to fit the data related to a pre-annealed initial state.

DISCUSSION

Obviously, a key point in the treatment resides in the determination of the parameters in equation (10). We intend to come back to this point in the future, after having selected for each of the three parameters the best measurements for the most accurate adjustment.

We have previously shown that, within experimental errors, the kinetics of yield and annealing processes were the same: any change in t_a or $\dot{\varepsilon}$ by the same factor has an equivalent effect on the yield stress[2]. Is that confirmed by the present theoretical results? Indeed, from (7), kinetics of the yield process may be expressed by:

$$[\mathrm{d}\sigma/AT/\mathrm{d}\ln\dot{\varepsilon} = 1]\mathrm{const.}T,\theta \quad (11)$$

while those of annealing may be derived from (4) as:

$$[\mathrm{d}\sigma_\theta/AT/\mathrm{d}\ln t_a = -C'\mathrm{d}\theta/\mathrm{d}\ln t_a]\mathrm{const.}T,T_a \quad (12)$$

By evaluating the slope of the isotherms in *Figure 6*, we found for equation (12) a numerical value which slightly varied with T_a from 1.1 at $T_a = 20°C$ to 0.97 at $T_a = 130°C$; hence, a mean value of 1.05 that must be compared with unity. Therefore, the present results confirm the previous experimental ones, but it is more appropriate to claim that the kinetics of both yield and annealing processes are nearly the same. This agrees with Struik's observations that the creep curves' shift rate is almost but not exactly unity[12].

The activation enthalpy of both processes differs somewhat: $Q_0 = 76$ kcal adjusted from tensile yield stress measurements[1,5] must be compared with 64 kcal used in the present investigation; also $C' = 0.768\,\mathrm{K}^{-1}$ differs from $C = 0.7\,\mathrm{K}^{-1}$. Although these values are close, it is impossible to fit the present data by taking the same value for C and C'.

As in equations (4), (6) and (10) no assumption was presupposed about the mechanical or thermal histories of the sample which have led to a given θ value. The model may be applied to other yield behaviours apart from the annealed rejuvenated ones. For example, let us assume that σ_θ denotes the tensile yield stress of a sample ice-quenched from above T_g. By combining equations (4) and (9), it is possible to determine the θ of the sample at room temperature (20°C), provided the yield stress is measured in the same conditions as σ_i. Such a value may be obtained using data reported previously[7]. In this case, θ was found to reach 421 K, a value which can be related to $t_a = 1.7 \times 10^6$ years using the response of equation (10) at 20°C. This means that at room temperature the yield stress of quenched samples does not vary, which has been already experimentally checked over a period of at least 3 years[13].

The θ variation given here may perhaps be useful in investigations of the brittle–ductile transition of annealed PC. A critical annealing temperature below which no noticeable annealing effect can be expected on the yield stress of 'as received' PC, may be determined from *Figure 6*, in the region of 80°C. At this temperature θ reaches θ_i and begins to decrease after about 1 month, entailing an increase in the yield stress. The same effect occurs after 2 months at 77°C and after 500 years at 60°C. As the decline in impact strength is closely related to the increase of the yield stress, the 80°C region may be considered as a minimum value of the annealing temperature to convert the 'as received' ductile PC form into a brittle one. Such a theoretical result agrees with the early observations of Allen *et al.*[14]

CONCLUSIONS

The present investigation succeeds in taking into account the effect of annealing on the yield stress of PC through an easy equation having a simple analytical expression. This equation may be applied to the yielding of any PC sample, whatever its mechanical or thermal history before annealing.

The parameters respectively attributed to the yield and annealing processes appear to be close but not identical.

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