Annealing of rejuvenated polycarbonate

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The effect of annealing mechanically rejuvenated samples of polycarbonate below T_g has been investigated by differential scanning calorimetry. All the traces exhibited a broad sub-T_g exotherm, preceded in some cases by a small sub-T_g endothermal peak. The position of the exotherm on the scan is strongly dependent on the annealing conditions. A method is proposed to obtain the value of the structural temperature characterizing any annealed rejuvenated sample, since in our opinion this is the chief quantity to be adopted in annealing investigations. Basic relations are chosen to be as simple as possible, containing only three parameters optimized using previous enthalpy relaxation data obtained on samples annealed after quenching. From the same relations, traces related to annealed rejuvenated samples are computed. The positions on the scan of calculated and experimental exotherms are compared and found to agree. Results tend to confirm that, to a first approximation, the annealing process does not depend on the sample treatment before annealing.

(Keywords: polycarbonate; annealing; rejuvenation; structural temperature; differential scanning calorimetry)

INTRODUCTION

In this paper we investigate through differential scanning calorimetry (d.s.c.) the structural evolution of rejuvenated samples of polycarbonate (PC) produced by annealing below T_g. Rejuvenation of the samples was obtained by cold pressing; such a strong deformation erases the effects of physical ageing[1], which are only partially removed by quenching in the case of PC.

The annealing behaviour of rejuvenated samples is shown to be similar to that of quenched samples previously studied[2], although the shapes of the d.s.c. traces related to the two types of sample are different. Quenched samples exhibit an endothermal peak at T_g while rejuvenated ones are characterized by a d.s.c. sub-T_g exotherm (which may be preceded by a small sub-T_g endothermal peak). These exotherms are shifted to higher temperatures with increasing annealing time t_a and annealing temperature T_a.

Previously[2,3], we have proposed that the chief quantity to be adopted in annealing investigations is θ, the structural temperature associated with a given annealing treatment. Let θ_i denote the structural temperature of an unannealed sample and subscripts q and r be related to quenched and rejuvenated samples respectively. For quenched samples, θ is always lower than θ_{iq} while the reverse is true for rejuvenated samples. The value of θ_{iq} has been accurately determined previously[2] from enthalpy relaxation data, but that of θ_{ir} is not available from direct measurements.

We propose here to use the same basic equations, chosen to be as simple as possible, to describe the annealing behaviour in both cases. Parameters are optimized by means of the previous data. The procedure adopted allows the determination of θ_{ir}, θ and the theoretical d.s.c. trace corresponding to any annealing treatment on rejuvenated samples.

EXPERIMENTAL

Samples

Rejuvenated samples (~10 mg) were machined from an extruded sheet of Makrolon (Bayer) and cold pressed from 2.08 to 0.88 mm (or at a lower ratio, from 1.30 to 0.74 mm for a few samples).

Annealing treatments

Annealing was performed inside the d.s.c. instrument for various times at three different temperatures below T_g: $T_a = 333$, 353 and 373 K. Heating to T_a and cooling from T_a to 296 K were conducted at 320 K min^{-1} and followed by d.s.c. scans.

Differential scanning calorimetry

Measurements were made with a Perkin–Elmer DSC-2C calorimeter at a fixed heating rate of 20 K min^{-1} from 300 to 460 K. Samples were then cooled at 320 K min^{-1} back to 296 K and a second scan was immediately recorded and taken as a reference for estimating the position of the exotherm.

DATA ANALYSIS

Examples of traces are given in *Figures 1* and *2*. For each sample, the dotted curve represents the scan taken as reference related to the quenched state (cooled to 296 K from above T_g at 320 K min^{-1}). Dotted and full curves are shifted vertically to match in their lower temperature part.

The full traces of *Figure 1* clearly reveal three characteristic features: a small sub-T_g endothermal peak (a), immediately followed by a broad exotherm (b) and a sharp exothermal peak (c) at T_g. Similar scans were obtained by Berens and Hodge[4] on cold drawn and cold

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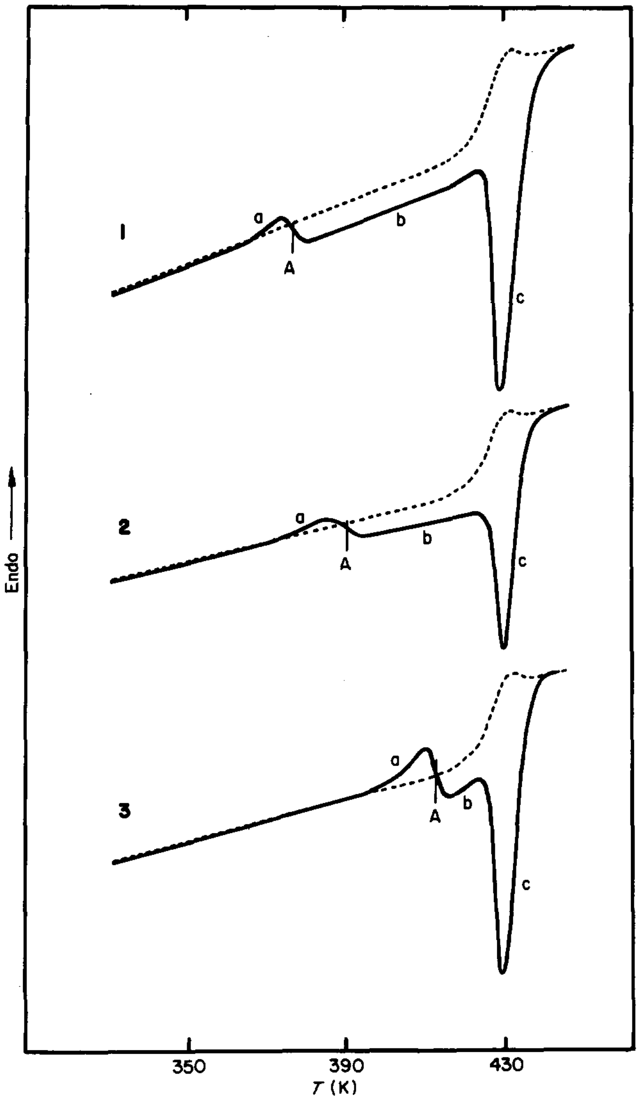

Figure 1 Examples of d.s.c. traces (full lines) obtained on rejuvenated samples after various annealing treatments: 16 h at 333 K (1); 2.4 h at 353 K (2); 7 h at 373 K (3). Dotted lines represent the second scan taken as reference. Rejuvenation treatment: cold pressing from 2.08 to 0.88 mm

pressed sheets of poly(vinyl chloride) (PVC) annealed below T_g.

The three characteristic parts a, b and c are also exhibited by traces related to a scanning rate of $10\,\mathrm{K\,min^{-1}}$. The onset of b lies about 5 K below that related to a scan obtained at $20\,\mathrm{K\,min^{-1}}$, but all other conditions remain unchanged.

Clearly, on some traces parts b and c do interfere, which prevents accurate enthalpy relaxation measurements in part b, given by the area enclosed between full and dotted scans (*Figures 1* and *2*). Only the onset of exotherm b can be accurately determined.

On traces related to samples annealed for short times and at low temperatures ($t_a \leq 1$ h at 333 and 353 K) or to unannealed samples, sub-T_g endothermal peaks are hardly perceptible or non-existent; examples are given in *Figure 2*. Berens and Hodge[4] have investigated the position and the magnitude of the sub-T_g endothermal peak of PVC as a function of T_a and t_a for a variety of thermal, mechanical and vapour treatments applied to the samples before annealing. They did not consider exotherm b.

On the contrary, we have followed the effect of annealing on the location of the exotherm on the d.s.c. trace and found a linear dependence as a function of ln t_a at constant T_a, there being no correlation with the presence or absence of a sub-T_g endothermal peak. Such a procedure allows investigation of a larger range of experimental conditions.

Let us point out that theoretical traces predicted from our treatment do not exhibit a sub-T_g endothermal peak; in our opinion, the striking feature in mechanical rejuvenation revealed by d.s.c. is exotherm b. We will come back to this point in the discussion.

And what about the exothermal peak observed at T_g? We found its magnitude varied randomly with t_a and T_a, as did Berens and Hodge[4], and we believe, in common with these authors, that it reflects the macroscopic recovery of the cold pressed samples and consequent changes in thermal contact with the calorimeter. No significant measurements can therefore be obtained from such a peak. In any event, its magnitude is always smaller for less pressed samples; for example, see scan 2 on *Figure 2*.

Thickness measurements were performed to check the

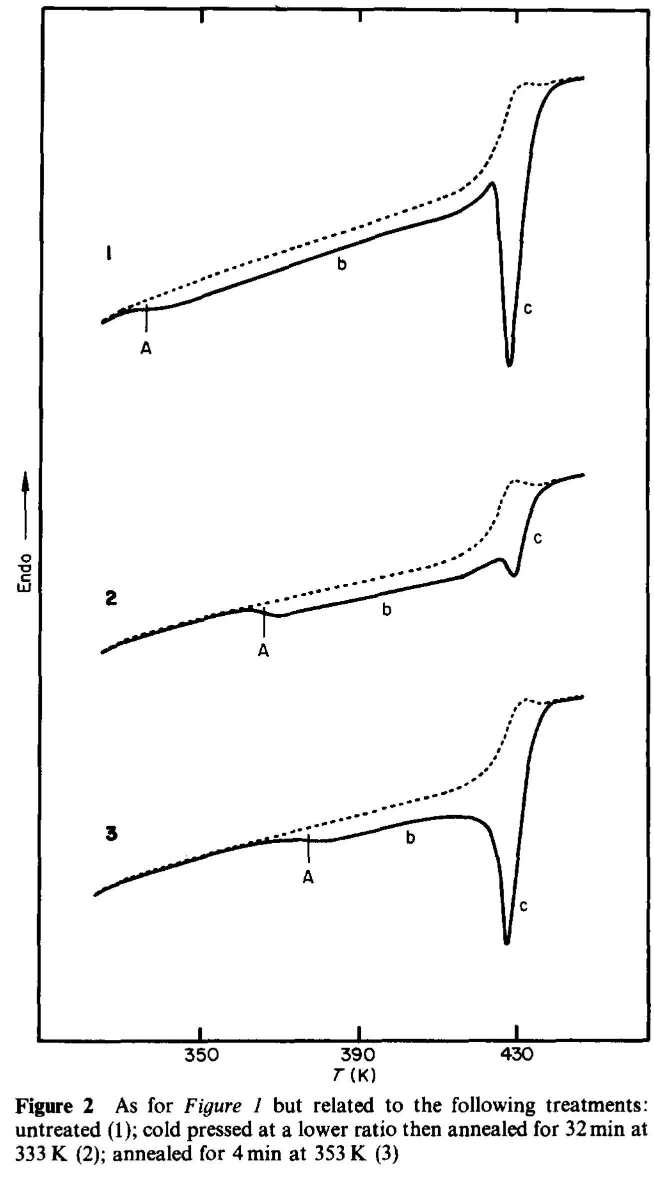

Figure 2 As for *Figure 1* but related to the following treatments: untreated (1); cold pressed at a lower ratio then annealed for 32 min at 333 K (2); annealed for 4 min at 353 K (3)

assumption of macroscopic recovery. Rejuvenated samples heated to temperatures below exotherm c and then cooled exhibited a small thickness recovery: about 0.001 and 0.0018 K^{-1} of their initial height (i.e. the height before pressing) for temperatures below and within region b respectively. On the other hand, samples heated to the maximum of exotherm c recovered about 0.15 K^{-1} of their initial height within the small temperature range (~ 5 K) related to the left part of exotherm c. This leads to a total recovery of 0.75 at the maximum, which allows us to think that this peak is due to the macroscopic recovery of the rejuvenated samples.

BASIC EQUATIONS

We believe that the annealing process consists, in any case, of configurational changes producing a decrease in θ. The differential equation of Davies and Jones[5], rewritten for θ at constant T_a, is chosen as previously[2,3] to express the annealing process:

$$d\theta = (T_a - \theta) J \, dt_a \qquad (1)$$

where J denotes the frequency of configurational change produced by annealing. The expression for J is voluntarily taken to be as simple as possible, containing the lowest number (namely three) of adjustable parameters, to avoid any ambiguity. The purpose is to show that the same expression may be used to describe the annealing of both quenched and rejuvenated samples, to a first approximation. More sophisticated expressions have been considered previously to describe annealing of 'as received'[3] and quenched[2] samples, which, all told, were hardly better fitted by the data than the present one. Thus J will be expressed as a function of a frequency factor v_0 and an exponential term containing the configurational entropy change ΔS and the activation energy Q:

$$J = v_0 \exp(\Delta S/R - Q/RT_a) \qquad (2)$$

where R denotes the ideal gas constant.

The following linear dependence between ΔS and θ will be assumed:

$$\Delta S/R = C(\theta - \theta_0) \qquad (3)$$

From (3), equation (2) may be rewritten as:

$$J = v \exp(C\theta - Q/RT_a) \qquad (4)$$

where the parameters v, C and Q need to be adjusted. For that purpose, previous data on enthalpy relaxation ΔH produced by annealing of quenched samples have been used. For a given treatment of such samples, the numerical integration of equation (1), at constant T_a, gives $\Delta\theta$, which may be linked to ΔH, through the following relation, which has previously[2] been established experimentally:

$$\Delta H = \Delta C_p(\theta - \theta_{iq}) = \Delta C_p \Delta\theta \qquad (5)$$

where ΔC_p denotes the heat capacity change occurring at T_g. Values of ΔC_p and θ_{iq} have been accurately determined previously[2]: $\Delta C_p = 0.056$ cal g^{-1} K^{-1}, $\theta_{iq} = 416.6$ K, $\theta_{ir} = 445$ K.

Each rejuvenated sample, annealed or not, is characterized by a given value of θ before testing in the d.s.c. The theoretical evolution of θ during the d.s.c. scan may be obtained from equation (1) by assuming that continuous heating at a rate v is replaced by a series of temperature steps ΔT, followed by isothermal holds of duration $\Delta t = \Delta T/v$. The differential equation becomes in this case:

$$d\theta = (T - \theta)(J/v) dT \qquad (6)$$

The d.s.c. scan gives, in fact, the evolution of $d\Delta H/dT$ as a function of T, which from (5) may be expressed by:

$$d\Delta H/dT = \Delta C_p d\theta/dT \qquad (7)$$

ADJUSTMENT OF THE PARAMETERS

Three parameters v, C and Q need to be adjusted. We have chosen for that purpose data obtained previously on quenched samples, which is given in *Figure 3* where ΔH is plotted as a function of $\ln t_a$ at constant T_a. Taking (5) into account, the numerical integration of equation (1) at constant T_a predicts curves with parallel linear parts. Such parallel parts are tried throughout the data, the slope being optimized by adjusting C. The horizontal distance between these parallel lines, linking data related to the same value of $\Delta\theta$ at different T_a, is adjusted to give the value of Q. Finally, the position of the response of equation (1) is adjusted to get the best fit to the data, which allows the determination of v.

Using the following numerical values of these parameters, $v = 10^{-95}$ s^{-1}, $C = 0.7$ K^{-1}, $Q = 64$ kcal mol^{-1}, equation (1) may be rewritten as:

$$d\theta = 10^{-95}(T_a - \theta)\exp\{0.7\theta - 3.2\,10^4(1/T_a)\} dt_a \qquad (8)$$

Full lines in *Figure 3* are calculated by numerical integration of (8), taking (5) into account; it can be seen on the graph that a satisfactory fit is found to the data obtained from annealing of quenched samples.

EXPERIMENTAL RESULTS

The position of exotherm b revealed on the d.s.c. experimental scan is investigated as a function of t_a and T_a.

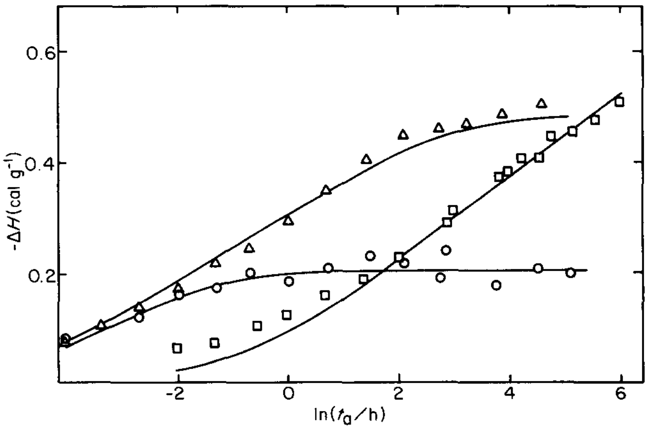

Figure 3 Enthalpy relaxation data obtained on quenched samples annealed for various t_a at $T_a = 383$ K (□), 408 K (△) and 413 K (○). Curves are calculated by numerical integration of equation (8), taking (5) into account

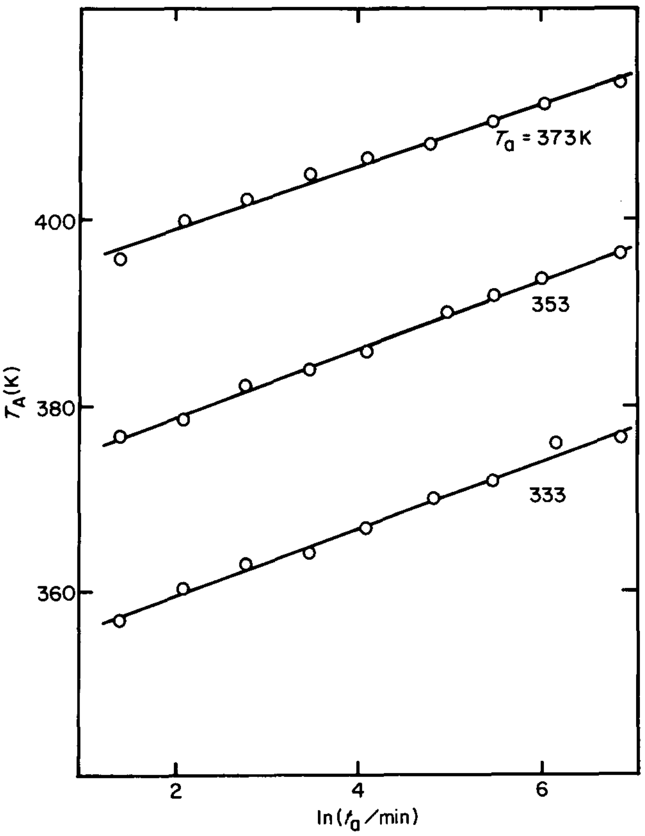

Figure 4 Plot of T_a as a function of ln t_a for three different annealing temperatures. Straight lines represent a best fit to the data

To determine this position, the inflexion at the beginning of the exotherm (point A on *Figures 1* and *2*) was arbitrarily chosen on the d.s.c. traces with or without endothermal peaks a. Let T_A be the related temperature. Results are plotted as a function of ln t_a for the three temperatures considered here (see *Figure 4*). Parallel straight lines on the graph represent a best fit to the data.

THEORETICAL RESULTS

Calculated d.s.c. traces

A theoretical d.s.c. trace related to an annealed rejuvenated sample characterized by a given value of $\theta > \theta_{iq}$ may be obtained to a first approximation by step-by-step numerical calculation of the following equation, which combines (6), (7) and (8):

$$\mathrm{d}\Delta H/\mathrm{d}T = (T-\theta)(\Delta C_p/v)10^{-95}\exp\{0.7\theta - 3.2\ 10^4(1/T)\} \qquad (9)$$

Various values of the step ΔT were tried; $\Delta T = 0.1$ K was found to give satisfactory results; smaller values did not increase the accuracy.

The temperature range within which the calculation has been carried out was chosen to obtain a constant value of $\mathrm{d}\Delta H/\mathrm{d}T$ in the lowest temperature part of the curve. The resulting curve exhibits an exotherm; examples are given in *Figure 5*. The procedure adopted cannot account for the sub-T_g endothermal peak revealed by some traces. On this point, experimental traces disagree with theoretical ones. A comparison is given as an example in *Figure 6*. For clarity, traces are magnified compared with those given in *Figures 1* and *2*. It can be seen on the graph that the value of T_A chosen to locate the exotherm on the experimental scan lies very near T_m, the temperature at the exotherm minimum on the calculated scan.

Determination of θ_{ir}

A set of theoretical scans may then be calculated until the curve is found which best fits the experimental trace related to the unannealed rejuvenated sample; the corresponding value is taken as θ_{ir} and is given below equation (5).

Determination of θ as a function of annealing conditions

From the estimate of θ_{ir}, the value of $\Delta\theta = \theta_{ir} - \theta$ may now be calculated as a function of t_a and T_a by numerical integration of (8) from θ_{ir} to θ, at constant T_a. Results related to the three values of annealing temperature considered here are given in *Figure 7*. Therefore, the proposed method is of use in obtaining the structural temperature characterizing any annealing treatment imposed on rejuvenated samples. This graph allows a value of θ to be associated with each value of T_A, and pairs of values t_a and T_a with each value of T_m.

COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

To test the validity of the proposed method of interpretation the annealing effects on rejuvenated samples, T_A (experimental) and T_m (theoretical full line), are plotted as a function of θ in *Figure 8*. A satisfactory agreement between both types of plot is observed.

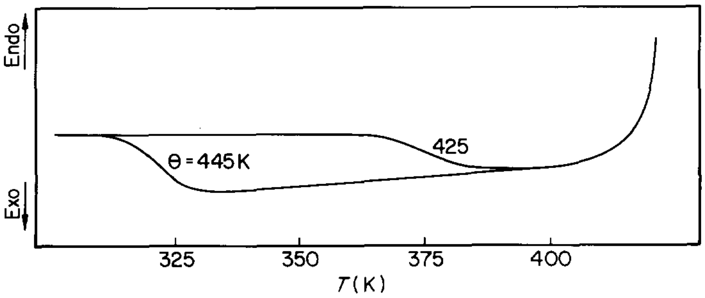

Figure 5 Examples of theoretical d.s.c. traces obtained by step-by-step numerical calculation of equation (9). The traces exhibit an exotherm

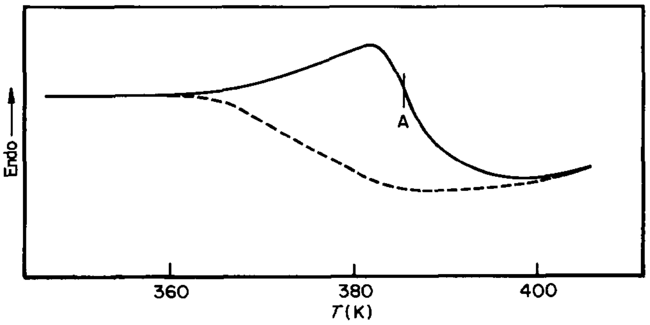

Figure 6 Experimental sub-T_g endothermal peak on a d.s.c. trace (full line) compared to the response of the model (dotted line) for a rejuvenated sample annealed for 1 h at 353 K and related to $\theta = 425$ K

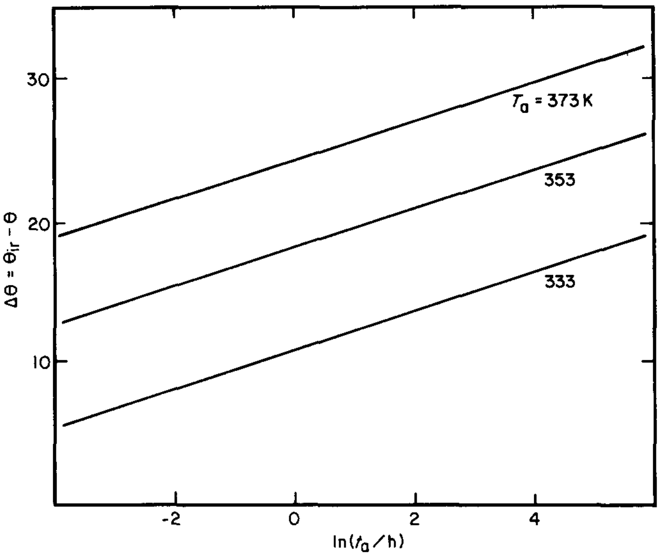

Figure 7 Plot of the calculated value of $\Delta\theta = \theta_{ir} - \theta$ as a function of ln t_a for the three annealing temperatures considered here

DISCUSSION

We first discuss the development of sub-T_g endothermal peaks (a) in the lowest temperature range of our d.s.c. traces. Berens and Hodge[4] suggest that these peaks, which they treat as a consequence of glass transition kinetics, may be a general feature of the annealing of glassy polymers. They consider that such peaks become the well known endothermal T_g overshoot for annealing temperatures within about 20 K below T_g. Hodge *et al.*[4,6,7,8] investigate sub-T_g peaks in PVC and T_g overshoots in various polymers. They propose a mathematical model which predicts an endothermal peak but cannot account for the possible development of an exotherm on the d.s.c. trace, i.e. the opposite of our treatment. In any case, the magnitude of the sub-T_g endothermal peaks is small compared to exotherms or T_g endothermal overshoots.

Our point of view leads us to explain the development of such peaks by referring to Kovacs' interpretation[9,10] of the observed volume maximum exhibited by isothermal volume relaxation of polymers submitted to a complex thermal history (downquenched from above T_g, then storage, followed by an upquench). The condition for the occurrence of a maximum is that there is a distribution of relaxation times. Kovacs has always assumed a one-to-one correspondence between volume relaxation and structural temperature. We have shown experimentally that such a relation exists between enthalpy relaxation and θ.

The mechanical and thermal history related to our samples may be compared to the thermal history of Kovacs' experiments: mechanical rejuvenation to obtain a mean value of θ as high as possible, then storage at T_a for time t_a, followed by heating in a d.s.c. Before testing, the sample may be considered as a set of cells, each characterized by its own kinetics and its own θ, in order to take into account the distribution of the θ values; the cells with the fastest kinetics have the lowest θ after annealing, and during the scan they will continue to evolve the fastest, since (as we agree with Kovacs) the cell kinetics are related to the mean value of θ. During the scan, when temperatures higher than T_a are reached, the θ values of the fastest cells will increase, which will lead through relation (7) to an endotherm in the d.s.c. trace. The mean θ of the sample moves towards higher values and the kinetics of the slowest cells accelerate. Beyond a critical value of T (namely T_A) and of θ, all the θ of the cells are higher than T_A and tend therefore to decrease, which entails an exotherm in the d.s.c. trace. In this view, the occurrence of the endothermal sub-T_g peak gives rise to the exotherm.

Secondly, we shall comment on the development of exothermal peaks at T_g. Without any doubt, such peaks spoil the trace and prevent the measurement of the area of the sub-T_g exotherm, as the two types of peak interfere. They are linked to the procedure we have adopted to rejuvenate our samples. We have chosen to cold press them only because it is an easy, rapid and effective way to obtain mechanical rejuvenation. Of course, to avoid this parasitic peak, rejuvenation must be obtained differently, for example by using samples which have been submitted to large plastic deformation in a simple shear test apparatus like that used by G'Sell *et al.*[11] This testing machine allows cycling of the specimen in plastic deformation in such a way that a complete recovery of the original shape of the specimen can be achieved. On retesting after one plastic cycle, the yield stress of the specimen is reduced by half, indicating a significant rejuvenation effect[12]; d.s.c. samples cut from such a cycled specimen may exhibit a trace with no exothermal peak at T_g.

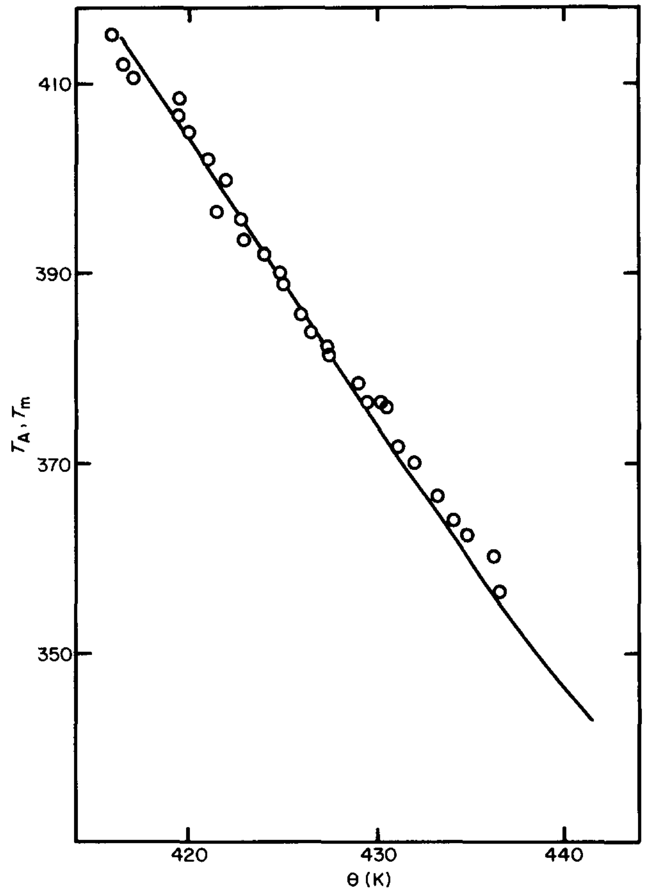

Figure 8 Plot of T_A as a function of θ compared to the variation of T_m (full line) determined from the related theoretical traces

CONCLUSIONS

Broad sub-T_g exothermal peaks observed on d.s.c. scans of mechanically rejuvenated samples of PC are shifted towards higher temperatures when the samples are pre-annealed below T_g. This shift is strongly dependent on the annealing conditions.

The annealing behaviour of rejuvenated samples, like that of quenched samples previously investigated, can be described by the same equation with the same values of the adjustable parameters. Correlation between experimental results and those calculated from this basic assumption is satisfactory. Therefore this behaviour does not appear to depend on the initial state of the sample at the start of the annealing process.

The proposed treatment allows determination of the value of θ related to a given annealed rejuvenated sample. Values of $\theta > \theta_{iq}$ (rejuvenated samples) characterize d.s.c. scans with an exothermal peak, while values of $\theta < \theta_{iq}$ (quenched or as-received samples) correspond to scans with a T_g overshoot.

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