Effect of physical ageing on enthalpy relaxation and isothermal contraction in bisphenol-A polycarbonate

Michel Washer

Physique des Matériaux de Synthèse, Université Libre de Bruxelles, 1050 Bruxelles, Belgium

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The intention of this paper is to correlate the decrease of free volume and the enthalpy relaxation which occur in high polymers during annealing. We used a simple correlation relation, with one chief parameter (the 'equilibrium temperature' θ), which can be deduced from different models. Data on polycarbonate (PC) show no correlation between enthalpy relaxation and isothermal contraction using that relation: the assumption that the decrease of free volume in PC in the glassy state obeys a Williams–Landel–Ferry (WLF) type equation could not be confirmed. Moreover, it seems that the changes of configuration occurring during annealing cannot be described with only one parameter.

(Keywords: polycarbonate; annealing; physical ageing; free volume)

INTRODUCTION

A model has been proposed by C. Bauwens-Crowet and J. C. Bauwens[1] assuming that both the yield process and the structural changes occurring during annealing may be expressed using equations characterized by the same free energy. It has also been assumed that both processes are identical: annealing consists in configurational changes occurring at zero stress. A satisfactory correlation between the enthalpy relaxation during annealing and the yield stress data on polycarbonate was found[1]. Moreover, it has been shown that the main parameter which depends on the thermal history of the sample is the entropy, which obeyed a WLF-type relation, expressed as a function of a structural temperature θ instead of the temperature T. θ was defined as the temperature at which the structure of a sample in a metastable state would be in equilibrium, and was supposed to fully characterize the structural state of the sample[1]. As the WLF relation is presumed to be linked to the free volume of the polymer, it should be possible to describe the isothermal contraction occurring during annealing using θ.

We intended to try and correlate this isothermal contraction and the enthalpy relaxation using θ as the chief parameter.

BASIC ASSUMPTIONS

Associating a structural temperature θ with each sample, the structural changes occurring during annealing will be characterized by $(\theta-\theta_i)$, where θ_i denotes the structural temperature of the untreated sample.

At constant temperature T_a, θ decreases with increasing duration t. We may use a basic differential equation already proposed by C. Bauwens-Crowet and J. C. Bauwens[1] analogous to that of Davies and Jones[2], and also used by Kovacs *et al.*[3]:

$$d\theta = -(\theta - T_a)J.dt \qquad (1)$$

where J is the frequency of configurational changes, which can be written:

$$J = J_0.\exp\left(\frac{\Delta S}{R} - \frac{Q_0}{R.T_a}\right) \qquad (2)$$

J_0 is a rate constant; Q_0 is the activation energy; ΔS is the change of configurational entropy, and has been shown to obey the WLF equation, expressed as a function of θ instead of T[1]:

$$\exp(\Delta S/R) = 10\left(\frac{17.44(\theta-\theta_i}{51.6+(\theta-\theta_i)}\right) \qquad (3)$$

From equations (2) and (3), equation (1) becomes:

$$d\theta = -(\theta - T_a)J_0 10\left(\frac{17.44(\theta-\theta_i}{51.6+(\theta-\theta_i)}\right)\exp\left(-\frac{Q_0}{R.T_a}\right)dt \qquad (4)$$

This treatment is quite satisfactory in describing enthalpy changes and increase in yield stress due to annealing[1].

The use of the WLF equation implies that the configurational changes during annealing produce a densification of the sample consistent with the decrease of free volume; therefore, any change of the material's properties would be linked to the decrease of specific volume Δv.

From the definition of θ, we can write:

$$\Delta H = (\theta - \theta_i)\Delta C_p \qquad (5)$$

where ΔC_p denotes the specific heat change occurring at the glass transition, and:

Present address: Solvay & Cie, rue du Prince Albert, 33, 1050 Bruxelles, Belgium

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$$\frac{\Delta v}{v}=(\theta-\theta_i)\Delta\alpha \qquad (6)$$

where $\Delta\alpha$ denotes the thermal expansivity change occurring at the glass transition.

Equations (5) and (6) can be deduced from a H (or v) as a function of T graph (*Figure 1*). Equation (5) can also be deduced from Petrie's treatment[4,5]. Let us point out that this correlation relation has also been proposed by Kovacs[6].

EXPERIMENTAL

Samples

Makrolon[c] (Bayer) (bisphenol-A polycarbonate) was used throughout with a viscosity average weight of 26 000. All samples were machined from the same extruded sheet.

Densitometric measurements were carried out on 1.00 g samples (discs, 0.2 cm thick, 2.3 cm diameter). Calorimetric measurements were carried out on 14 mg samples (discs, 0.08 cm thick, 0.45 cm diameter). Reference samples were untreated samples.

Thermal treatments

We used two samples for each treatment. The samples were annealed at 111°C, 119°C and 130°C, for durations from 2 to 256 h.

Densitometric measurements

Hydrostatic weighing was chosen. The liquid used was water, with addition of 5% detergent to break the surface tension. We used a 0.7 l flask, placed on the balance, so that thermic gradients could be neglected. The sample was linked to the balance by a 0.2 mm diameter glass fibre.

Using calculations derived from Ratcliffe's treatment[7], the relative decrease of free volume was given by:

$$\frac{\Delta v}{v}=\frac{v_r-v_e}{v_r}=1-\frac{m_{ar}(m_{ae}-m_{le})}{m_{ae}(m_{ar}-m_{lr})} \qquad (7)$$

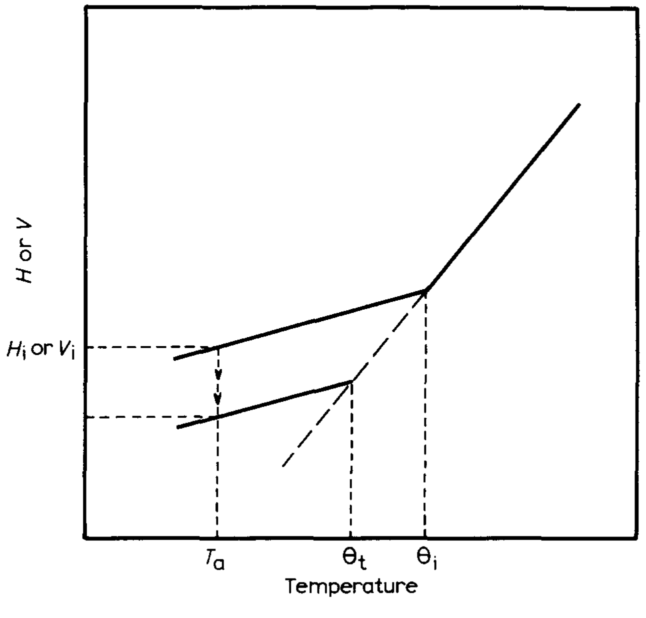

Figure 1 Specific enthalpy (H) or specific volume (v) as a function of the temperature (T). The subscript 'i' denotes the initial state, the subscript 't' denotes the state of the annealed samples. 'T_a' is the annealing temperature

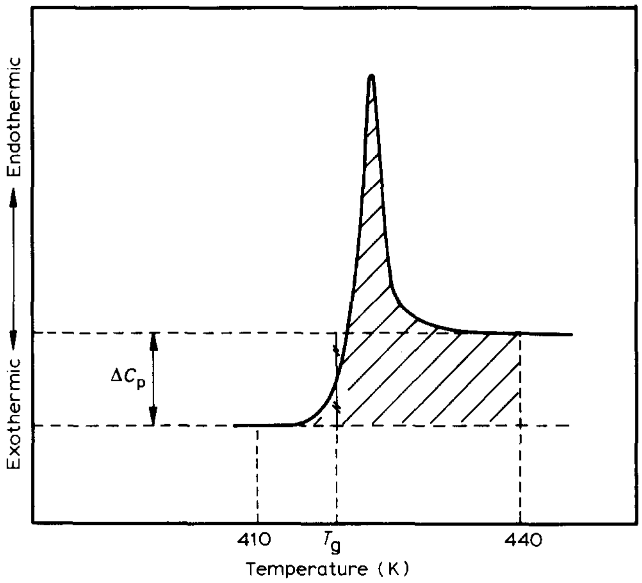

Figure 2 Determination of the glass transition temperature (T_g), the specific heat change occurring at the glass transition (ΔC_p), and the enthalpy relaxation. The striped area is the area measured for the determination of the enthalpy relaxation

where v_r and v_e are the specific volumes of the reference and the treated sample, m_{ar} and m_{ae} are the weights in air of the reference and the treated sample, m_{lr} and m_{le} are the weights in liquid of the reference and the treated sample.

The absolute error on $\Delta v/v$ was 0.00002.

Calorimetric measurements

A Perkin-Elmer DSC II instrument was used, with a heating rate of $20\,\mathrm{K\,min^{-1}}$. Enthalpy relaxation was obtained by measuring the area between the d.s.c. trace and the extrapolation of the baseline obtained for temperatures below the glass transition temperature T_g, between 410 K and 440 K, as shown in *Figure 2*, and by deducing from this area the area measured for the reference samples. Reproducibility was checked by comparing areas measured for different untreated samples: the differences did not exceed 1.4%.

RESULTS

In *Figures 3*, *4* and *5* we have plotted the values of $\Delta\theta$ deduced from calorimetric and from densitometric measurements.

The values deduced from calorimetric measurements were given by equation(5), using $\Delta C_p = 0.053\ \mathrm{cal\ g^{-1}\ K^{-1}}$ (an average value obtained from our d.s.c. traces). The determination of ΔC_p is shown in *Figure 2*.

The values deduced from densitometric measurements were given by equation (6), using $\Delta\alpha = 3.44\times10^{-4}\ \mathrm{K^{-1}}$, as obtained by Zoller[8].

The values of $\Delta\theta$ given by densitometric measurements are about four times lower than those given by calorimetric measurements.

We checked the accuracy of the measurement methods. The scattering of the experimental points is that of the original samples.

D.s.c. measurements agree with those obtained by C. Bauwens-Crowet and J. C. Bauwens[1], and with those obtained by Petrie and Marshall[6].

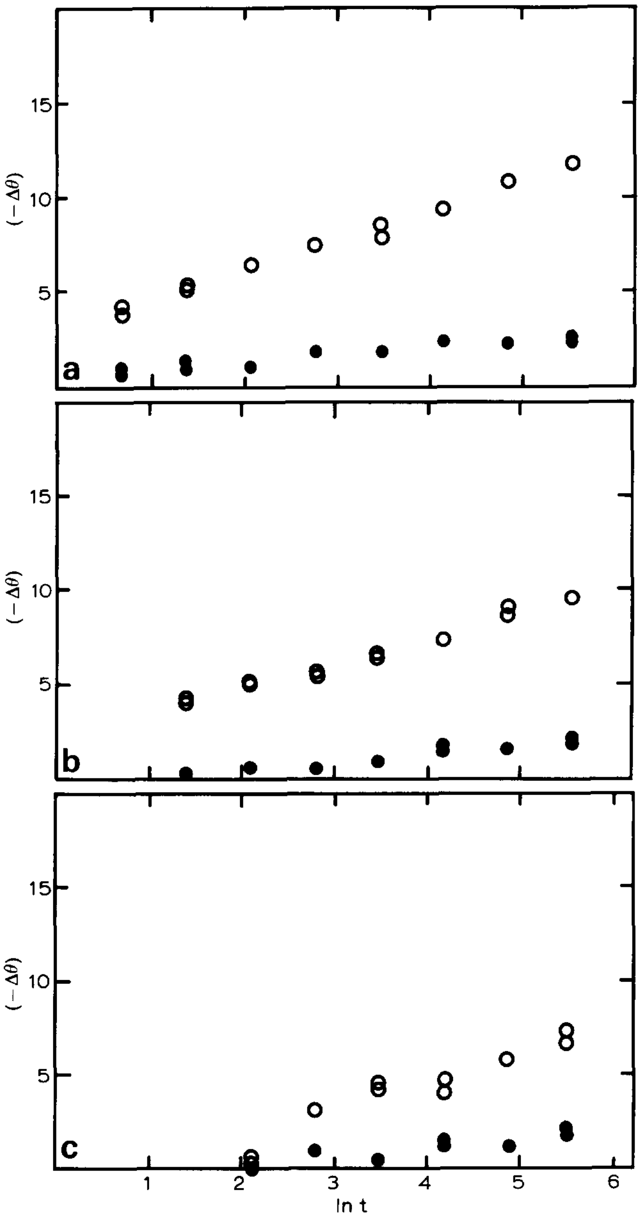

Figure 3 Change in structural temperature ($-\Delta\theta$) as a function of the natural logarithm of the time (t). (a) $T=130$°C; (b) $T=119$°C; (c) $T=111$°C; $\Delta\theta$ is in °C; t is in hours. (○): deduced from calorimetric measurements. (●): deduced from densitometric measurements

Densitometric measurements agree with those obtained by Morgan and O'Neal[9], within experimental errors; we obtain the same saturation value as Legrand[10], but with a different time constant. It must be noted that Legrand conducted his measurements on PC from a different origin (Lexan©). This might account for the difference in relaxation times.

DISCUSSION

The model we have described was used successfully in correlating enthalpy relaxation and yield stress increase after annealing[1]. Our measurements show that there seems to be no correlation between these and isothermal contraction.

This implies that the use of the WLF equation in describing the evolution of the configurational entropy in the glassy state cannot be justified by a theory based on the decrease of free volume, although this equation seems proper. The decrease of free volume is far too low to justify such a change in enthalpy or yield stress.

The universal values of the constants of the WLF equation, i.e. 17.44 and 51.6, depend on the structure of the material, but these values cannot be justified in the glassy state by the decrease of free volume.

Moreover it seems that more than one parameter is needed to describe the structural changes occurring in the glassy state; changes occur which affect the enthalpy (and the mechanical properties) without much affecting the free volume.

CONCLUSIONS

Enthalpy, and mechanical properties, are affected by annealing, but the evolution of these properties cannot be linked to a decrease of the free volume. The configurational entropy changes, which have been shown to obey the WLF equation expressed as a function of a structural temperature θ instead of the temperature T[1], cannot be explained by a theory based on free volume in the polymer.

Structural changes occur in the glassy state which affect enthalpy without substantially affecting the free volume; it seems that a one parameter theory cannot successfully describe the physical changes occurring during annealing or physical ageing.

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REFERENCES

1 Bauwens, J. C. and Bauwens-Crowet, C. *Polymer* 1982, **23**, 1599
2 Davies, R. O. and Jones, G. O. *Proc. Roy. Soc.* 1953, **A217**, 26
3 Kovacs, A. J., Hutchinson, J. M. and Aklonis, J. J. in 'The Structure of Non-Crystalline Materials', (Ed. P. H. Gaskell), Taylor and Francis, 1977, p. 153
4 Petrie, S. E. B. *J. Polym. Sci. A-2* 1972, **10**, 1255
5 Marshall, A. S. and Petrie, S. E. B. ACS Symposium Series, (Ed. R. K. Eby), 1979, **95**, 245
6 Kovacs, A. J., Hutchinson, J. M. and Aklonis, J. J. in 'Proceedings of the Symposium on the Structure of Non-Crystalline Materials', Cambridge, Sept. 1976
7 Ratcliffe, R. T. *Brit. J. Appl. Phys.* 1965, **16**, 1193
8 Zoller, P. *J. Polym. Sci. Polym. Phys. Edn.* 1982, **20**, 1453
9 Morgan, R. J. and O'Neal, J. E. *J. Polym. Sci.* 1976, **14**, 1053
10 Legrand, D. G. *J. Appl. Polym. Sci.* 1969, **13**, 2129