On the physical significance of Bucci relaxation times obtained from thermal sampling

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It is shown that the Bucci relaxation time, τ_B, is not in general a true measure of a physical relaxation time in a mechanical or dielectric thermal sampling (TS) experiment. A method is proposed by which τ_B may be corrected to obtain an effective relaxation time, $\tau_{B\frac{1}{2}}$, which is the relaxation time computed from the Bucci equation at 50% relaxation: $\tau_{B\frac{1}{2}}$ when correctly calculated, depends only on the temperature of observation. The calculation is based on two assumptions: (i) that the shape of the distribution of relaxation times (slope of the ramp) has been assessed within the experimental error; (ii) that the shift factor is the same for all relaxation times within the narrow packet activated in the TS experiment. It is shown by experiment that the plot of log τ_B *versus* T^{-1} for a viscoelastic polymer (isotactic polypropylene in the β-region) is curved: the curvature is explained theoretically. The plot of log $\tau_{B\frac{1}{2}}$ *versus* T^{-1} yields a straight line, in agreement with the Arrhenius equation. The early TS experiments, which have been interpreted to favour the compensation rule, should be re-analysed since the published analysis is made by Arrhenius plots using uncorrected values of τ_B. The high temperature TS experiments on polystyrene and polypropylene (stated to be anomalous by Lacabanne and co-workers in yielding curved log τ_B *versus* T^{-1} plots) will be found, when analysed by the methods described in this paper, to conform to the Arrhenius equation.

Keywords Mechanical relaxation; dielectric relaxation; thermal sampling; Bucci relaxation times; viscoelastic polymer

INTRODUCTION

In this paper we examine the use of the equation of Bucci and Fieschi[1,2] for determining the relaxation time in thermal sampling experiments. The method of thermal sampling is of great potential and is one of the two methods most likely to resolve the dominant outstanding problem in polymer viscoelasticity. This is the question of whether or not the compensation rule[3,4] applies to the activated processes within a given relaxation. There is increasing evidence that it does. The time honoured and theoretically convenient assumption of thermoviscoelasticity, that for all processes within a given relaxation the activation energy ΔH is constant[5], is therefore under attack.

The attack comes from two quarters. First, from a recent determination of ΔH within a given relaxation using the extremely precise method of double T-jump[6]. Second, from the method of thermal sampling, (TS).

In TS a viscoelastic strain (or, in the alternative experiment, a dielectric polarization) is frozen into the specimen by a rapid quench to a low temperature T_0. The release of the frozen-in strain (or polarization) is then observed as the specimen is heated in a controlled manner: the most convenient heating programme is T linear in time t,

$$T = T_0 + pt. \tag{1}$$

The different variants on this experiment have been lucidly reviewed by van Turnhout[7].

The most commonly used TS experiment is the temperature window variant. In a temperature window experiment a constant stress is applied at T_σ, for a time t_σ, commonly of order 1000s. The temperature is then lowered by ΔT to T_d, *Figure 1*: ΔT is the temperature window and is usually about 10K. At T_d the stress is removed and the specimen permitted to recover partially for a time t_d, usually equal to t_σ. The specimen is then quenched (by 50K or so) to T_0 so that viscoelastic strain is frozen-in at T_0. A linear heating run is then performed and the decay of the frozen-in strain, $\gamma(t)$ observed as a function of time. Since $\gamma(t)$ is observed it may be differentiated to yield $\dot{\gamma}(t)$. According to the Bucci equation the ratio $\gamma(t)/\dot{\gamma}(t)$, a quantity with the dimensions of time, is a relaxation time typical of the relaxing system. We denote it τ_B,

$$\tau_B = \frac{\gamma(t)}{\dot{\gamma}(t)}. \tag{2}$$

From equation (2), τ_B is known as a function of time t in the experiment and is known therefore as a function T from equation (1): $\dot{\gamma}(t)$ is negative and should be written $|\dot{\gamma}(t)|$: we follow the conventional shorthand as in equation (2).

In a dielectric TS experiment with temperature window, an electric field is applied to the specimen at T_σ for a time t_σ: the temperature is then dropped by ΔT to T_d and the field removed for a time t_d. The specimen is then quenched to T_0 and the polarization consequently frozen-in. During the following heating run (equation (1)) the discharge

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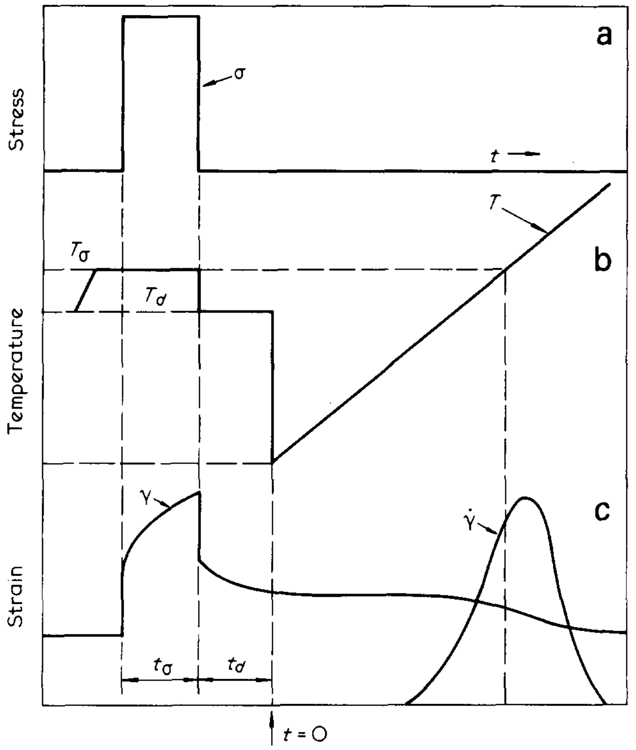

Figure 1 Description of the thermal sampling experiment (temperature window variant). The specimen is stressed at T_σ for t_σ: the temperature is lowered to T_d and the stress removed for t_d. The specimen is then quenched to T_0. Experimental time t takes its zero at this point and the specimen is heated linearly, equation (1): during the heating γ and hence $\dot{\gamma}$ are measured

current $j(t)$ is measured with an electrometer and the Bucci equation[1] is,

$$\tau_B = \int_t^\infty j(u)\,\mathrm{d}u / j(t).$$

The phenomenological theory for the dielectric and linear viscoelastic experiments are, of course, identical.

The Bucci relaxation time, τ_B, we shall take to be an operational quantity obtained from experiment or from model calculation using the Bucci equation (equation (2)). Previous workers have accepted the validity of τ_B as a characteristic relaxation time of the relaxing system and have determined the Arrhenius constants, ΔH and τ_∞ from a plot of $\log \tau_B$ against T^{-1}. Arrhenius plots obtained in this way have not shown parallel lines as would be the case if ΔH was constant. Rather they have shown straight lines fanning out from a point. This result has been interpreted as favouring the compensation rule, according to which the i^{th} relaxation time, τ_i, of the distribution of relaxation times depends on temperature according to[3],

$$\tau_i = \tau_c \exp \frac{\Delta H_i}{R}\left[\frac{1}{T} - \frac{1}{T_c}\right] \tag{3}$$

The values of ΔH_i differ systematically for each τ_i but T_c is the same. Equation (3) is referred to as the compensation rule and T_c the compensation temperature; at $T = T_c$ all relaxation times take the same value τ_c, so that at T_c the specimen conforms to the Debye equations, with a single relaxation time. It is reported that T_c is close to the glass transition temperature, T_g: this highly significant observation is based on the applicability of the Bucci equation, which was used both in the mechanical[3] and in the dielectric[4] experiments.

The compensation rule has been found in other systems, notably at the Zener relaxation in the alloy Ag–24 atomic % Zn[8]. The possibility of a compensation temperature, at which the solid conforms to the Debye equations has been discussed by Macdonald[9] and by Nowick and Berry[10]. The possibility of a proportionality between ΔH and the entropy of activation ΔS also follows from the theories of Wert and Zener[11] and Eby[12]. The proposal therefore that the compensation rule applies to polymeric mechanical and dielectric relaxation, although certainly radical, is not entirely unexpected. Nevertheless, there is a weak point in the TS evidence, which is the lack of a theory relating the Bucci relaxation time, as determined operationally, with the distribution of relaxation times governing the relaxation process.

The purpose of the work described here was to examine the physical content of the Bucci equation. This is done both by model calculation and by experiment. The stress-temperature-time programme adopted for the calculation and for the experiment is shown in *Figure 2*. The stress is applied at T_σ for t_σ and the specimen maintained at that *same* temperature for an additional time t_d under zero stress before quenching. This much reduces the problem of calculation when compared to the temperature window experiment, and has the same physical effect. The temperature window experiment has been analysed theoretically by Zielinski and Kryszewski[13]. Their model is the same as ours but the object of their calculation is different. The purpose of the work described here is to relate the operationally defined Bucci relaxation time to a relaxation time of the relaxing system. The Bucci plot, $\log \tau_B$ against T^{-1} is then corrected. The way this is done

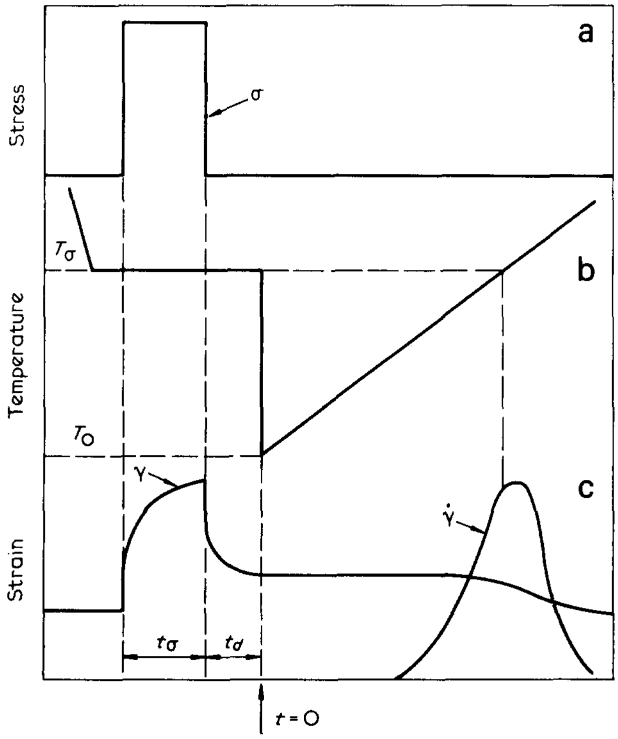

Figure 2 Description of thermal sampling experiment (isothermal loading and unloading variant). The position of the zero in the experimental time t is indicated

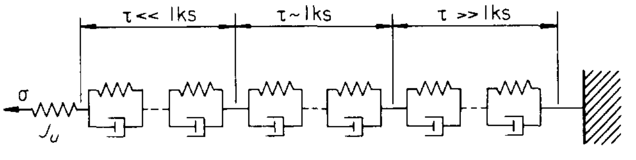

Figure 3 Voigt model: the loading pattern t_σ = 1.2 ks, t_d = 0.18 ks leaves strain in the packet of elements at $\tau \sim 1$ ks (see *Figure 4*). The Hookean component (J_u) and the long and short relaxation time components are unstressed

is described in the following section. The analysis is for a viscoelastic experiment but the results are applicable to any relaxation phenomenon such as thermoluminescence or dielectric relaxation described by analogous linear equations.

MODEL CALCULATION

Consider a Voigt model, *Figure 3*, with elements of equal strength J distributed three per decade from $\tau = -\infty$ to $+\infty$. This closely spaced line spectrum replicates the continuous spectrum of relaxation time typical of polymers: we do not suggest that the real spectrum consists of isolated lines. The same calculation can be performed for a continuous spectrum but with more difficulty, a loss of physical insight and precisely the same result. There is also a loss of flexibility if the continuous spectrum is adopted, which becomes serious when the calculation is made with a wedge-distribution (see Discussion section). The conclusions of the model are not changed by increasing the density of elements above three per decade. It may be helpful to the reader to remark at once, that the loading pattern activates in the TS experiment only those relaxation elements with τ in the region of 1 ks. Thus the mathematically convenient assumption of an infinitely wide box-distribution is physically reasonable, since the parts of the distribution far removed from 1 ks play no part in the analysis.

We confine the theoretical calculation to the analysis of a particular experiment which was performed, and is described in the Experimental section: in this experiment the stress σ is applied for $t_\sigma = 1200$s and then removed for $t_d = 180$s. It is a trivial problem to repeat the calculation for other loading and unloading patterns. Consider the i^{th} element precisely at the time in which the specimen is to be quenched, *Figure 2*. The strain in this element is, by the Boltzmann superposition principle,

$$\gamma_i = \sigma J[1 - \exp -(t_\sigma + t_d)/\tau_i] - \sigma J[1 - \exp -(t_d/\tau_i)] \quad (4)$$

which for the values of $t_\sigma = 1200$s and $t_d = 180$s yields,

$$Z_i = \frac{\gamma_i}{\sigma J} = \exp -(180/\tau_i)[1 - \exp -(1200/\tau_i)] \quad (5)$$

The fraction Z_i is the ratio of the strain remaining in the i^{th} element at the instant of quench to the maximum possible strain within that element, which is σJ.

The relaxation times in the model are equally distributed three per decade; so that, for instance, between 1s and 10s elements occur at 1.0s, 2.154s, 4.6415s and 10s. For this line spectrum of infinite width the values of Z_i calculated from equation (5) which are sensibly finite, lie at times between 21.54s and 10^5s and are recorded in *Figure 4*. In passing we note that the potential of the TS technique is illustrated in *Figure 4*. The loading pattern has placed within the specimen a strain which is essentially confined to relaxation times in a narrow band between 10^2 and 10^4s. This strain is to be frozen-in by quenching: the kinetics of its release are to be observed. The problem is, of course, the detailed analysis of the strain release. The method of correcting from a box-distribution (equal J) to a ramp-distribution is described in the Discussion section.

Isothermal strain release at T_σ

Consider first the strain release subsequent to time t_d if the specimen is *not* quenched but maintained at T_σ. In the i^{th} element the strain at time t is,

$$\frac{\gamma_i(t)}{\sigma J} = Z_i \exp -(t/\tau_i), \quad (6)$$

in which we take here (and in the remainder of the paper) the zero in t at time t_d after the stress is released, as indicated in *Figure 2*. The total strain at time t, $\gamma(t)$, is

$$\frac{\gamma(t)}{\sigma J} = \Sigma Z_i \exp -(t/\tau_i). \quad (7)$$

Hence the ratio of the strain at time t to the strain at $t = 0$, $\gamma(0)$, is,

$$\frac{\gamma(t)}{\gamma(0)} = \frac{\Sigma Z_i \exp -(t/\tau_i)}{\Sigma Z_i}. \quad (8)$$

This quantity is plotted for the model in *Figure 5*.

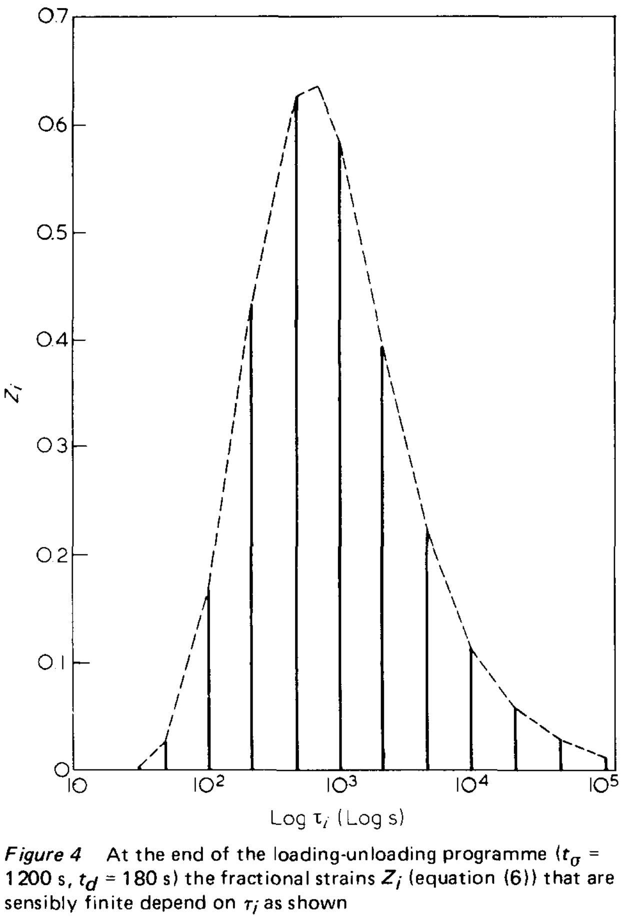

Figure 4 At the end of the loading-unloading programme (t_σ = 1200 s, t_d = 180 s) the fractional strains Z_i (equation (6)) that are sensibly finite depend on τ_i as shown

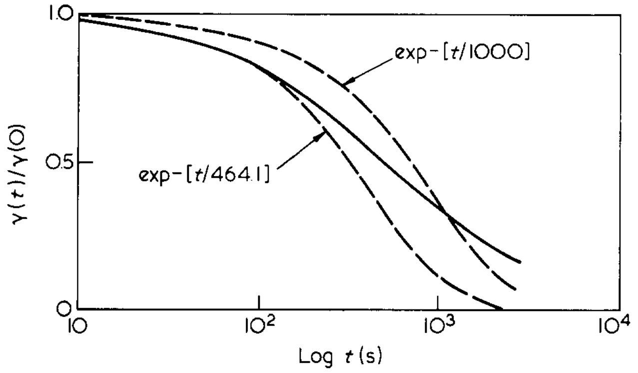

Figure 5 Dependence at T_σ of $\gamma(t)/\gamma(0)$ on log t for the model after the imposed loading (t_σ = 1200 s) and unloading pattern (t_d = 180 s). Also plotted is $\gamma^1(t)/\gamma^i(0)$ for the two dominant relaxation times (see *Figure 4*) at τ = 464.1 s and τ = 1000 s. Zero of experimental time t is indicated in *Figure 2*

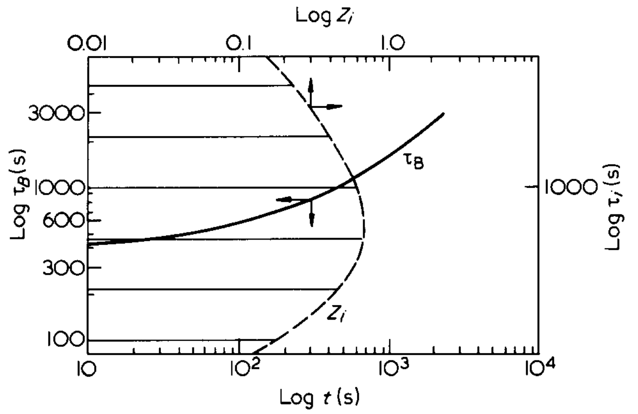

Figure 6 Isothermal dependence of the Bucci relaxation time τ_B at T_σ on log t (scales to the left and below). Also shown is the value of Z_i for the dominant relaxation times (scales to the right and above)

The function given in equation (8) and plotted in *Figure 5* is a sum of exponentials each weighted by an appropriate Z_i. The dominant values of Z_i are for the two relaxation times 464.1s and 1000s (see *Figure 4*). The functions $\exp-(t/464.1)$ and $\exp-(t/1000)$ are also plotted in *Figure 5* and represent the decay of the strain in the two dominant viscoelastic elements. The function, equation (8), for the model has the general appearance of an exponential decay but is in fact broader.

Application of the Bucci equation (equation (2)) to the model can be made easily since by differentiating equation (8) we have from equation (2),

$$\tau_B(t)=\frac{\gamma(t)}{\dot{\gamma}(t)}=\frac{\Sigma Z_i \exp-(t/\tau_i)}{\Sigma Z_i(1/\tau_i)\exp-(t/\tau_i)} \qquad (9)$$

Values of $\tau_B(t)$ computed from equation (9) are plotted in *Figure 6* against log t. It will be seen that $\tau_B(t)$ increases monatonically from 435s at $t = 10$s to 2880s at $t = 2300$s. Now for a particular element, the i^{th}, the ratio of the instantaneous strain in the elements to the instantaneous strain rate,

$$\frac{Z_i \exp-(t/\tau_i)}{Z_i(1/\tau_i)\exp-(t/\tau_i)}=\tau_i, \qquad (10)$$

is naturally independent of t. The calculated τ_B of the model equals the relaxation time of the two dominant elements, *Figure 6*, at $t = 30$s (464.1s element) and at $t = 459$s (1000s element). So whilst the observed τ_B passes through the range of the dominant relaxation times, it cannot ever be a precise measure of them without correction.

One obvious way of making a correction is to examine the plot of $\tau_B(t)$ against $\gamma(t)/\gamma(0)$, which is shown in *Figure 7*. The calculated τ_B varies from 418s at $\gamma(t)/\gamma(0)=1.0$ to 2880s at $\gamma(t)/\gamma(0)=0.187$. Suppose we arbitrarily define the 'effective relaxation time' of the model (under the given loading pattern) to be the value of τ_B at $\gamma(t)/\gamma(0)=0.5$. Other definitions are possible and lead to an equivalent result. At $\gamma(t)/\gamma(0)=0.5$ the effective relaxation time is $\tau_{B\frac{1}{2}}=$ 1040s, *Figure 7*. Let the correction factor for the Bucci relaxation time determined at t, $\tau_B(t)$, be $\alpha(t)$,

$$\alpha(t)=\frac{\tau_{B\frac{1}{2}}}{\tau_B(t)}=\frac{1040}{\tau_B(t)}: \qquad (11)$$

$\alpha(t)$ is plotted against $\log\gamma(t)/\gamma(0)$ in *Figure 7*. Now suppose only a fragment of the relaxation curve is observed so that at a specific time t_1 we know $\gamma(t_1)$ and $\dot{\gamma}(t_1)$: it then follows that

$$\tau_B(t_1)=\frac{\gamma(t_1)}{\dot{\gamma}(t_1)}. \qquad (12)$$

The correction factor $\alpha(t_1)$ is known from $\gamma(t_1)/\gamma(0)$ (*Figure 7*) so that the effective relaxation time $\tau_{B\frac{1}{2}}$ is,

$$\tau_{B\frac{1}{2}}=\alpha(t_1)\tau_B(t_1). \qquad (13)$$

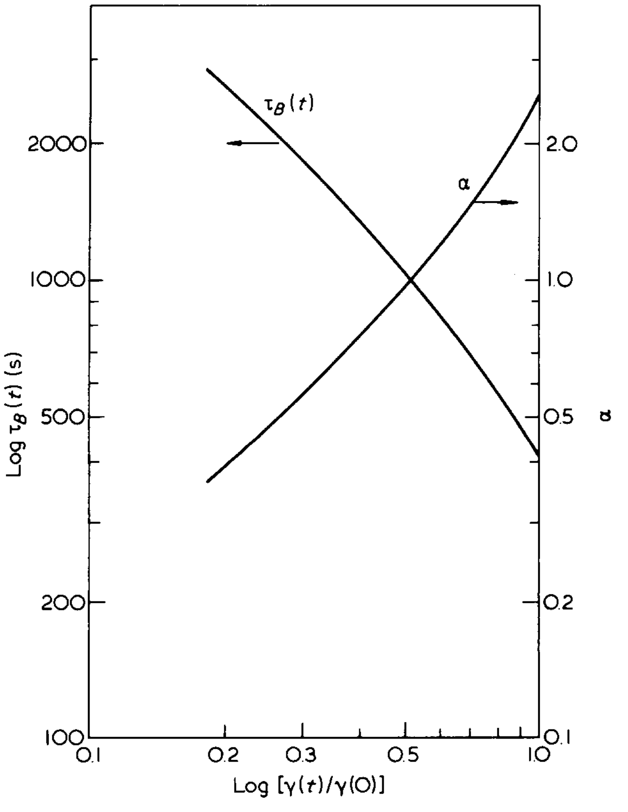

Figure 7 Isothermal dependence of the Bucci relaxation time $\tau_B(t)$ at T_σ on the value of $\gamma(t)/\gamma(0)$. Also shown (scale to the right) is the dependence of the correction factor, $\alpha(t)$ on $\gamma(t)/\gamma(0)$, (see equation (11))

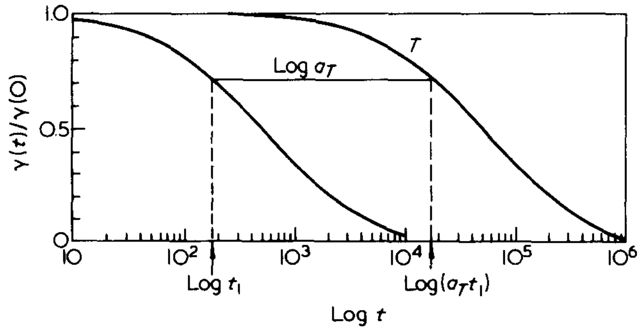

Figure 8 Illustration of equation (19) showing isothermal dependence of $\gamma(t)/\gamma(0)$ on log t for the loading pattern $t_\sigma = 1200$ s, $t_d = 180$ s at T_σ, zero in t taken from this point. Experiment 1, recovery at T_σ: experiment 2, recovery after an instantaneous T-jump at $t = 0$ from T_σ to temperature T such that log $a_T = 2$

Thus if at any temperature we know $\gamma(t)$ and $\dot{\gamma}(t)$, for a specific loading and unloading pattern we can obtain the effective relaxation time. The value of this correction will become apparent when we consider the *non-isothermal* release of frozen-in strain.

Isothermal strain release at T

Before considering the decay of strain induced by the temperature programme given by equation (1) (see *Figure 2*), consider the relationship between the $\gamma(t)$ curves for the model when (1) the specimen is left at T_σ to recover (equation (8) gives this recovery curve): and (2), at $t = 0$ a temperature jump is performed from T_σ to T and the specimen maintained at T. The loading histories are otherwise identical up to the point $t = 0$ (stress on at T_σ for t_σ and off at T_σ for t_d). The T-jump, T_σ to T causes the i^{th} relaxation time at T_σ, $\tau_i(T_\sigma)$ to change instantaneously to $\tau_i(T)$,

$$\tau_i(T) = a_T \tau_i(T_\sigma): \tag{14}$$

and, for an Arrhenius system,

$$a_T = \exp \frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_\sigma}\right]. \tag{15}$$

For the narrow packet of relaxation times activated by the loading programme we take a_T to be effectively constant. Even for a distribution obeying the compensation law, we take the packet to be sufficiently narrow so that, within experimental error, the approximation of equal a_T for the packet is reasonable. The data can be tested to determine the precision of this assumption.

In the first experiment (isothermal strain release at T_σ) the strain at a particular time t is,

$$\gamma^{T_\sigma}(t) = \sigma J \Sigma Z_i \exp - [t/\tau_i(T_\sigma)] \tag{16}$$

In the second experiment at temperature T and at time $a_T t$,

$$\gamma^T(a_T t) = \sigma J \Sigma Z_i \exp - [a_T t / a_T \tau_i(T_\sigma)], \tag{17}$$

therefore

$$\gamma^T(a_T t) = \gamma^{T_\sigma}(t). \tag{18}$$

Now these experiments have identical loading histories so that $\gamma(0)$ is the same for each.

Hence,

$$\frac{\gamma^T(a_T t)}{\gamma(0)} = \frac{\gamma^{T_\sigma}(t)}{\gamma(0)} \tag{19}$$

The two relaxation curves are therefore identical when plotted against log t, except that they are separated along the log t axis by log a_T, as indicated in *Figure 8*.

Now from these two recovery curves we can calculate from the Bucci equation values of τ_B: at T_σ and time t from equation (9),

$$\tau_B^{T_\sigma}(t) = \frac{\Sigma Z_i \exp - [t/\tau_i(T_\sigma)]}{\Sigma Z_i [1/\tau_i(T_\sigma)] \exp - [t/\tau_i(T_\sigma)]}. \tag{20}$$

At T and time $a_T t$,

$$\tau_B^T(a_T t) = \frac{\Sigma Z_i \exp - [a_T t / a_T \tau_i(T_\sigma)]}{\Sigma Z_i [1/a_T \tau_i(T_\sigma)] \exp - [a_T t / a_T \tau_i(T_\sigma)]} \tag{21}$$

It follows therefore that,

$$\tau_B^T(a_T t) = a_T \tau_B^{T_\sigma}(t): \tag{22}$$

equation (22) follows from equation (21) because a_T is taken to be constant for the narrow packet of relaxation times activated by the stress history. It follows also, that,

$$\tau_{B\frac{1}{2}}^T = a_T \tau_{B\frac{1}{2}}^{T_\sigma}. \tag{23}$$

Now suppose we know at temperature T_σ values of $\alpha(t)$ (see equation (14)): this quantity will be known precisely from the imposed loading and unloading pattern. Dividing equation (23) by equation (22),

$$\frac{\tau_{B\frac{1}{2}}^T}{\tau_B^T(a_T t)} = \frac{\tau_{B\frac{1}{2}}^{T_\sigma}}{\tau_B^{T_\sigma}(t)} \tag{24}$$

The quantity on the right-hand side, is by definition $\alpha(t)$, equation (11). It follows therefore that if the parameter $\alpha(t)$ is known at T_σ for values of $\gamma(t)/\gamma(0)$, from 1 down to 0, then these same values of α hold at any arbitrary temperature T for the same values of $\gamma(t)/\gamma(0)$. For example, if at T_σ at $\gamma(t)/\gamma(0) = 0.8$, $\alpha = 1.88$ (*Figure 7*) then at an arbitrary temperature T (for the same loading pattern) it follows that when $\gamma(t)/\gamma(0) = 0.8$, α also equals 1.88: α is determined uniquely at any temperature by the value of fractional strain remaining, $\gamma(t)/\gamma(0)$. This fact, although not particularly of use in isothermal recovery, permits a valuable correction of the raw τ_B^T data in the TS experiment, as we show next theoretically and by experiment.

Non-isothermal release of strain

Consider the specimen to have followed the stress–temperature programme of *Figure 2* ($t_\sigma = 1200$s, $t_d = 180$s) and that it is on the heating run at temperature T given by equation (1), and that the time is t. Both $\gamma(t)$ and $\dot{\gamma}(t)$ are measured and hence although the specimen is only instantaneously at T we may still compute,

$$\tau_B^T(t) = \frac{\gamma^T(t)}{\dot{\gamma}^T(t)} \tag{25}$$

We require, however, the value of the effective relaxation

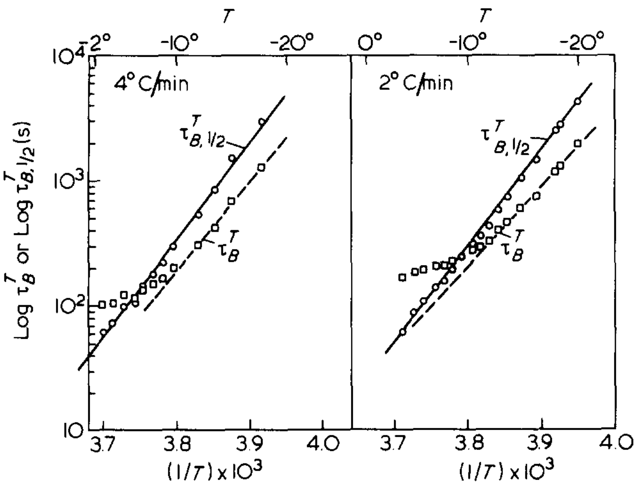

Figure 9 Bucci relaxation times plotted log $\tau_B{}^T(t)$ against T^{-1} (squares) for heating rates 2° C/minute and 4° C/minute. Also shown is the effective relaxation time (computed from $\tau^T_B(t)$ using a box-distribution) plotted log $\tau^T_{B1/2}$ against T^{-1} (circles)

time at T, $\tau^T_{B\frac{1}{2}}$. This is easily found, since we know the value at (T, t) of $\gamma^T(t)/\gamma(0)$: hence we know from the calculated curve, (*Figure 7*) the appropriate value of α: hence the value of $\tau^T_{B\frac{1}{2}}$ follows,

$$\tau^T_{B\frac{1}{2}} = \alpha \tau^T_B(t) \tag{26}$$

Thus for all values of T at which $\gamma(t)$ and $\dot{\gamma}(t)$ are determined we obtain the effective relaxation time at that value of T. From equation (23) it follows that,

$$\frac{\mathrm{d}\ln \tau^T_{B\frac{1}{2}}}{\mathrm{d}(1/T)} = \frac{\mathrm{d}\ln a_T}{\mathrm{d}(1/T)} \tag{27}$$

which from equation (15) yields,

$$\Delta H = 2.301R\,\frac{\mathrm{d}\log \tau^T_{B\frac{1}{2}}}{\mathrm{d}(1/T)}. \tag{28}$$

An experimental test of this method of correcting raw data in thermal sampling experiments is given in the following section.

EXPERIMENTAL

The specimen was a thin blade of isotactic polypropylene (Propathene PXC 8830) received from ICI. Its density at 20°C was 0.905 g ml^{-1}. Before machining the polymer was annealed at 130°C and slowly cooled. It was mounted in a torsional creep machine[14] and surrounded by a cavity through which nitrogen gas was passed at the required temperature. The thermostatically controlled nitrogen gas was generated by a method based on that of Schwippert and van der Waal[15]. The temperature of the gas was controlled with a programmable three term controller.

The purpose of the experiment was to check the theoretical correction procedure outlined in the Model Calculation section and not, in this instance, to examine the compensation rule. We elected to study at temperatures in the β-region, just below T_g. The specimen was cooled from room temperature to −20°C (at 8°/minute) and maintained at that temperature under zero stress for 20 minutes. The specimen was then stressed for 20 minutes (t_σ). The stress was then removed for 3 minutes (t_d) and the specimen at once quenched to −50°C (T_0). The time dependence of the strain was observed as the specimen was heated from −50° to +20°C at a rate of 2°/minute. As the torsional strain in the specimen decreased the suspension of the torsional creep machine rotated back towards its zero position. This rotation was amplified by an optical lever and recorded on a Graphispot. It was observed that a very small temperature induced rotation of the specimen occurred (probably due to thermoelastic stresses) in the absence of strain recovery. In order to allow for this small rotation, the specimen (under zero stress throughout) was put through the identical temperature programme and the rotations measured with the Graphispot. This permitted small experimental zero corrections to be made to recovery strains. A second pair of experiments was then performed identical in every way except that the heating rate from $T_0 = -50°$ was 4°/minute.

Values of $\tau^T_B(t)$ were obtained and are shown in *Figure 9* plotted log $\tau^T_B(t)$ against T^{-1}. It will be seen that the data conform more or less to a straight line at low temperatures but curve off into a flat region at high temperatures. The point at which the data curve off differs between the two heating rates. Values of $\tau^T_{B\frac{1}{2}}$ were calculated as described in the Model Calculation section and are plotted also in *Figure 9*. The essential point about the correction is that the data is transformed from a curve on the T^{-1} plot to a straight line.

DISCUSSION

We regard the analysis of the Model Calculation section as being so entirely rational, and its success in converting the curved log τ_B *versus* T^{-1} plot into standard Arrhenius form so striking, that a comparable procedure should be adopted in future for all Bucci relaxation times.

Further evidence in favour of the correction is the difference in the position of the bend in the plot of log τ^T_B *versus* T^{-1} with heating rate. The value of τ_B obtained at T *should* be independent of heating rate, a point made originally by Bucci, Fieschi and Guidi[2]. That the bend depends on heating rate is clear evidence that the raw data (τ^T_B) is not a true measure of a physical relaxation time of the system.

The procedure outlined in the Model Calculation section can be improved by taking into account the fact that the relaxation times are not of equal strength. The first advance in precision is to assume that the distribution is wedge-shaped and to obtain the slope of the wedge using the method advanced by Ferry[16]. This is done by differentiating a creep curve obtained at T_σ: a double-logarithmic plot of creep rate *versus* time yields the slope of the wedge. Then from the wedge slope values of $\tau_B(t)$ can be calculated and from these a new set of $\alpha(t)$ appropriate to the wedge slope. This was done and the wedge $\alpha(t)$ correction applied to the raw data: the results are shown in *Figure 10*. The values of ΔH obtained are given in *Table 1*.

It will be seen from *Table 1* that the agreement between the values of ΔH for the two rates of heating is remarkable. This precision is an intrinsic virtue of the TS technique. The discrepancy between the values calculated from the raw data at the two heating rates is probably due to the

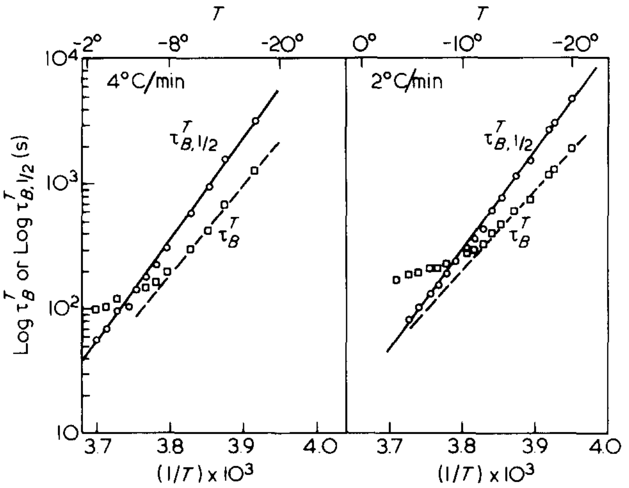

Figure 10 Bucci relaxation times plotted log $\tau^T_B(t)$ against T^{-1} (squares, same data as in *Figure 9*) for heating rates 2°C/minute and 4°C/minute. Also shown is the effective relaxation time computed using a ramp-distribution plotted log $\tau^T_{B1/2}$ against T^{-1} (circles)

Table 1 Values of ΔH in kcal mol^{-1} obtained from Arrhenius plots: stressing temperature $T_\sigma = -20°C$. We take the best values to be those in the third column: the percentage deviations of the second and first columns from the third are indicated. For the raw, uncorrected data, the log τ_B *versus* T^{-1} plot is curved: the value of ΔH shown is obtained from the low temperature portion (see *Figures 9* and *10*). Model used for correcting the raw data has three elements per decade

		Corrected data: $\tau_{B1/2}$	
Heating rate	Raw data: τ_B	Box distribution	Wedge distribution
2°/min	29.3 (−20%)	35.0 (−5%)	36.7 (0%)
4°/min	32.6 (−11%)	35.0 (−5%)	36.7 (0%)

difficulty of selecting the cut-off point. A more elaborate model with ten elements per decade was also used for the correction and yielded values of ΔH for the 2°/min and 4°/min experiments as follows; 35.4 and 35.3 kcal mol^{-1} for the box distribution; 37.7 and 37.6 kcal mol^{-1} for the ramp distribution. We take these values to be more reliable than the values from the model with three elements per decade.

Whether or not the extra work in using the wedge is necessary depends on the precision required. The slope of the ramp and the direction of slope are, in general, temperature dependent. It follows that the discrepancy between the box and the wedge values of ΔH will vary in magnitude and also in sign with the stressing temperature T_σ. For most purposes the wedge should be used. The correction procedures can be performed quickly by computer.

Another method (if neither box nor wedge is considered adequate) is to determine α in a separate isothermal experiment at T_σ. The specimen is put through its normal loading and unloading cycle and strain recovery observed at T_σ. Values of τ_B at T_σ are then calculated at values of $\gamma(t)/\gamma(0)$ in the range of interest.

The bend in the log $\tau^T_B(t)$ *versus* T^{-1} plot for the raw data shown in *Figure 9* has been described by Zielinski and Kryszewski[13]. At low temperatures the data conform more or less to a straight line (see *Figure 9*). This coincides with the region in which $\gamma(t)/\gamma(0)$ is above 0.5, in which region the raw τ_B data provides a reasonable but not precise measure of the dominant relaxation times. It will be noted from *Figure 6* that in this region τ_B does not depend too heavily on t and it is this fact that causes the log $\tau^T_B(t)$ *versus* T^{-1} plot to be more or less linear at low temperatures. When the value of $\gamma(t)/\gamma(0)$ moves below 0.5, τ_B commences to vary rapidly with log t and it is this which causes noticeable bend in the data shown in *Figure 9*. Values of ΔH obtained by differentiating the low temperature portion of the raw log τ_B *versus* T^{-1} plot are given in *Table 1*. They are of order 17% lower than the values from the wedge correction. The literature values of ΔH for various polymers obtained by TS using both mechanical[3] and dielectric[4] techniques use low temperature data only (τ^T_B), as indicated in *Figures 9* and *10*. It is certain that the interpretation of curved log τ_B plots *versus* T^{-1} in polystyrene[17] and in polypropylene[18] in terms of the Vogel equation is incorrect: the appropriate course is to re-analyse this data using the method proposed in this paper.

We are at present using this corrected thermal sampling technique to study the variation of ΔH with relaxation time in the β-region in order to compare with the observations made by double T-jump on the α-region[6]. The results will be reported elsewhere.

The extent of the error induced by the assumption of a constant α_T for the activated packet we take up elsewhere. It obviously depends on the peak width, which is under the control of the experimenter, and on the rate of variation of ΔH with relaxation time.

The values of t_σ (1200s) and t_d (180s) adopted were quite arbitrary and were selected to suit experimental conditions. It is possible to probe other parts of the spectrum by using other values of t_σ and t_d, whilst maintaining the same ratio of t_σ/t_d. There is a limit to the value of t which is convenient: it would probably be possible to go up × 100 in both t_σ and t_d and down in both by × 10. A more likely experimental programme with the same objective involves keeping t_σ and t_d constant but varying T_σ. This is the experiment, in the temperature window variant, which has been performed by Lacabanne *et al.*[3] and by Zielinski, Swiderski and Kryszewski[4] using the uncorrected Bucci equation. In order to establish the validity of the compensation rule and the placing of T_c close to T_g, these experiments should also be re-analysed using a correction of the form proposed in this paper.

CONCLUSION

The method proposed for correcting Bucci relaxation times is entirely rational and is supported by experiment.

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