

The kinetics of the α relaxation in an amorphous polymer at temperatures close to the glass transition

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The kinetics of the α relaxation of a crosslinked copolymer of acrylonitrile and butadiene ($T_g = -7^\circ\text{C}$) were studied in the temperature range ($T_g + 17^\circ\text{C}$) down to ($T_g - 8^\circ\text{C}$). The techniques used were shear creep analysed by time-temperature ($t-T$) superposition and thermal sampling (TS) with correction procedures proposed by McCrum. In this range the kinetics do not follow the compensation rule, as had been proposed in the pioneering TS experiments by Zielinski, Swiderski and Kryszewski and by Lacabanne *et al.*. The McCrum correction removes a discrepancy between the pioneering TS experiments and the conclusions of classical $t-T$ superposition experiments. The methods of TS and $t-T$ superposition are compared. At low temperatures, below ($T_g + 3^\circ\text{C}$), the TS method is superior: $t-T$ superposition is unreliable due to lack of normalization and to the physical ageing perturbation. At temperatures from ($T_g + 3^\circ\text{C}$) to ($T_g + 11^\circ\text{C}$) $t-T$ superposition is highly reliable since normalization is not required and there is no ageing. At temperatures above ($T_g + 11^\circ\text{C}$) the precision of $t-T$ superposition depends on the validity of the normalization procedure. It has yet to be determined whether or not the compensation rule applies at temperatures below ($T_g - 8^\circ\text{C}$): the method most likely to settle this important question is TS, mechanical or dielectric variant, with McCrum correction for the distribution of relaxation times.

Keywords Relaxation kinetics; thermal sampling; creep; time-temperature superposition

INTRODUCTION

The onset of microbrownian motion of the polymer backbone is the origin of the dramatic change in properties which occurs near the glass transition^{1,2}. Theoretical understanding of the kinetics of varied physical phenomena—mechanical, dielectric, volume and enthalpy relaxation for example¹⁻³—is based on experimental observation of the temperature dependence of the governing relaxation times. At temperatures above T_g there are structural changes which are reflected in volume changes, frequently and convincingly rationalized in terms of free-volume, or holes: these structural effects dominate the changes in relaxation time brought about by temperature change. But below and near T_g when structural changes are reduced, and at the lower temperatures eliminated, the relaxation times exhibit a temperature dependence which is not understood. There has been in fact no consensus even as to the appropriate experimental procedure.

The new technique of thermal sampling (TS) provides a welcome new experimental attack. In TS a narrow packet of the distribution of relaxation times is stimulated by an imposed specific electric field or mechanical stress history. The recovery kinetics of this narrow packet of relaxation times is then observed experimentally. The TS mechanical technique has been used to study the kinetics of the α -process in three amorphous polyolefins by Lacabanne *et al.*⁴. They reported the kinetics to follow the compensation rule: the temperature dependence of the i th relaxation time τ_i is given by:

$$\ln \tau_i = \ln \tau_c + \frac{\Delta H^i}{R} \left[\frac{1}{T} - \frac{1}{T_c} \right] \quad (1)$$

T_c , the compensation temperature and τ_c are constants. Each elemental τ_i of the distribution is governed by the Arrhenius equation with specific activation enthalpy ΔH^i : the distribution exists because ΔH^i is distributed. When $T = T_c$ all the values of τ_i are the same and equal τ_c , *Figure 1a*. It was observed that T_c lay just above T_g , the glass transition temperature ($T_c = T_g + 27^\circ\text{C}$) and that $\tau_c = 0.7$ s. This result was supported by a study, using the dielectric variant of TS, by Zielinski, Swiderski and Kryszewski⁵ who observed in amorphous poly(methyl methacrylate) that T_c lay just below T_g ($T_c = T_g - 10^\circ\text{C}$) with $\tau_c = 0.25$ s.

This would of course be a sensational observation if substantiated, since at temperatures above the glass transition temperature of an amorphous polymer, when the volume is in thermal equilibrium, the α relaxation times have in the past always been observed to follow the equation of Williams, Landel and Ferry (WLF)^{1-3,6}. According to the WLF equation the i th relaxation time at temperatures T and T_0 takes the values τ^i and τ_0^i :

$$\tau^i = a_T \tau_0^i \quad (2)$$

$$\log a_T = - \frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (3)$$

C_1 and C_2 are constants. The distribution occurs because the τ_0^i are distributed: the shift factor a_T is the same for all relaxation times, *Figure 1b*. Experiment has shown the WLF equation to hold at high temperature but to fail below T_g .

In the glassy state below T_g all observations—apart from TS—concur in showing a departure from WLF which commences at $T \sim T_g$ (possibly as high as $T_g + 10^\circ\text{C}$). The rate of increase of relaxation time with

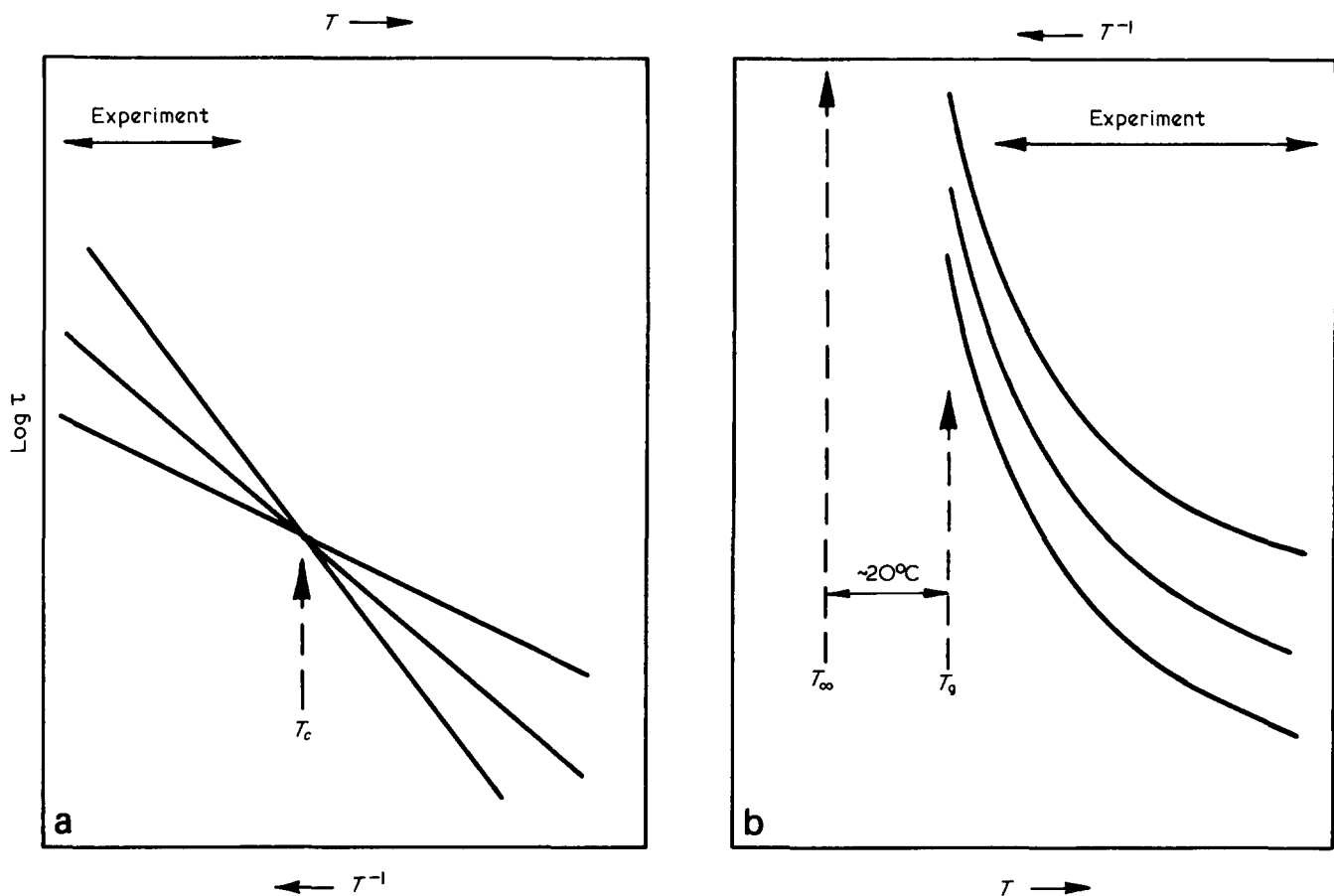


Figure 1 Illustration of the temperature dependence of three relaxation times selected arbitrarily from the α relaxation distribution of an amorphous polymer according to: (a) the compensation rule, equation (1), plotted against T^{-1} . The distribution changes shape so that at the compensation temperature all relaxation times take the value τ_c . Observations place $T_c \sim T_g$. (b) Williams, Landel and Ferry, equation (3), plotted against T . At T_∞ , approximately 20°C below T_g , all relaxation times are predicted to equal infinity. The temporal separation between the relaxation times remains constant: the distribution does not change shape with change of temperature. The best experimental support for the WLF equation comes from experiments performed at $T > T_g + 10^\circ\text{C}$

decreasing temperature is systematically reduced as the temperature is reduced: the temperature dependence of the shift factor $\log a_T$ has been observed, both in mechanical and dielectric relaxation, to be a sigmoid following the WLF equation at temperatures above T_g and then, from a point of maximum ($d \log a_T/dT$), bending over into a curve of gradually reducing slope in the glassy region. There are many reports of this in the literature over the past thirty years, some of which have been recorded in review texts² (see in particular Sommer⁷ and Saito and Nakajima⁸).

The difference between the TS experiment and the large number of classical observations might perhaps be attributed to a difference in the magnitudes of the observed relaxation times. In the TS experiments the observed relaxation times are of order 1 ks: in the work of Ferry and co-workers¹, for example, they are $\sim 10^5$ times lower. In consequence, the experiments of Ferry and co-workers were conducted at temperatures above T_g , whereas TS experiments were conducted, for the most part, below T_g , as indicated in Figure 1. It might then be argued that the WLF equation holds above T_g —where it is supported by observations also taken above T_g —and that the compensation rule holds below T_g , in which temperature range it is supported by the TS experiments. The TS experiments are however in conflict with a large number of step function experiments taken below T_g which probe relaxation times as long, or longer, than those probed in

the TS experiments. These step function experiments are, however, of unquantified validity—as we will describe later—on the substantial ground that there is evidence that for $T < T_g$ the distribution of relaxation times changes shape, that the experiments are perturbed by physical ageing and that it is impossible at present to normalize the data correctly before analysis.

The experiments described in this paper were conducted to resolve the discrepancy. The BFG plot, used both by Zielinski *et al.*⁴ and Lacabanne *et al.*⁵ in the TS data analysis, can be erroneous. In the work to be described here, TS experiments were performed on an amorphous polymer above and below T_g and the data corrected by the procedures described by McCrum⁹. It was possible with the same apparatus and the identical specimen to study the relaxation kinetics in the same temperature region using shear creep step function experiments and this was done. The work therefore had two main objectives, a study of the kinetics of the α -relaxation in an amorphous polymer, and a comparison of the TS and shear creep techniques.

There was an intention also to examine the validity of the method of time-temperature ($t-T$) superposition, which in the latest shear creep experiments^{10,11}, has been applied to the raw data without normalization of any kind. The purpose of normalization as used by the early workers, Ferry¹, Tobolsky and co-workers¹² for example, is well known: the intention is to eliminate a perturbation

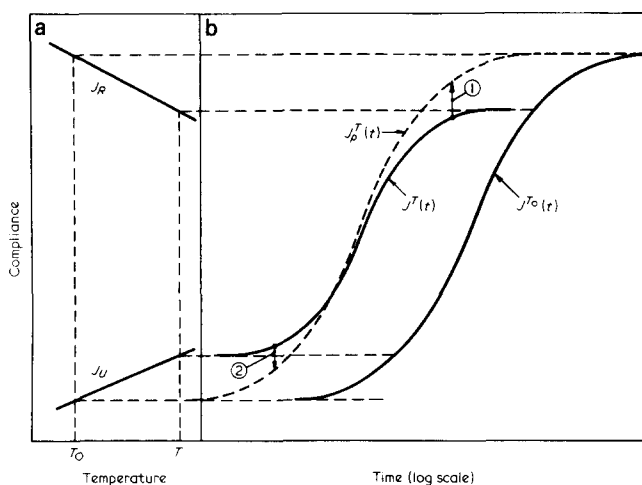


Figure 2 Idealized diagram showing the effect of the temperature dependencies of J_U^T and J_R^T on the creep compliance for the α -relaxation of an amorphous polymer. (a) Plot of J_U^T and J_R^T against temperature: (b) dependence of $J^T(t)$ and $J^{T_0}(t)$ on log time. The vectors (1) and (2) indicate how the normalization described by equation (8) transforms $J^T(t)$ into $J_p^T(t)$, which is the curve which may be superposed by horizontal shift upon $J^{T_0}(t)$ to yield $\log a_T$

due to the temperature dependence of the limiting compliances. It seemed correct therefore, whilst subjecting the TS technique to a searching scrutiny, to examine also the consequences of the use of un-normalized data in t - T superposition.

The polymer system selected for study was a cross-linked copolymer of butadiene and acrylonitrile with a glass transition of -7°C . The experimental region of interest lay just below room temperature, which meant that the specimen, when stored overnight mounted in the apparatus at room temperature, was relaxing in the rubbery state: in this way all experiments started from the same equilibrium, relaxed state. A crosslinked system was chosen to eliminate the terminal dispersion¹⁰. The low water affinity of this copolymer was important in permitting a simple experimental design. The choice of a copolymer increases somewhat the difficulty of a molecular interpretation of the experiment. It seemed far more important at this stage however, to secure a reliable and reproducible experiment and for this reason a crosslinked stable copolymer was selected for study. There is reason to suppose that the outline behaviour deduced for the kinetics of the α -relaxation in a copolymer will apply also to the α -relaxation of homopolymer.

THEORY

In this section we review those elements of relaxation theory which are pertinent to the α -relaxation of a crosslinked amorphous polymer: for a full account of the background see Ferry¹ and McCrum, Read and Williams².

Time-temperature superposition

The form of the temperature dependence of the limiting compliances for the glass-rubber relaxation is shown in Figure 2a: increasing temperature decreases J_R (an entropy elastic effect) whereas J_U increases (an energy elastic effect). Defining the temperature dependence by the coefficients, b_T, c_T, d_T ^{13,2}:

$$J_R^T - J_U^T = b_T (J_R^{T_0} - J_U^{T_0}) \quad (4)$$

$$J_U^T = c_T J_U^{T_0} \quad (5)$$

$$J_R^T = d_T J_R^{T_0} \quad (6)$$

The distribution of relaxation times at $T, \phi^T(\ln \tau)$ is taken to be related to the distribution at T_0^2 :

$$\phi^T(\ln \tau) = \phi^{T_0}(\ln \tau/a_T) \quad (7)$$

a_T is the shift factor (compare equation (2)). Implicit in equation (7) is the constancy of a_T for all elements of the distribution. Thus at once t - T superposition is impossible if the compensation rule holds (equation (1), Figure 1a).

The purpose of t - T superposition is to measure a_T : it is essential to eliminate the temperature dependence of the limiting compliances so that they do not perturb the measurement. For illustration, Figure 2b shows two creep curves, one at T_0 and the other at $T, (T > T_0)$. The change from T_0 to T causes (i) the inflection in the creep curve to shift to shorter values of t : (ii) the lower asymptote of the creep curve at T, J_U^T , to lie above $J_U^{T_0}$: the upper asymptote, J_R^T , to lie below $J_R^{T_0}$, as indicated in Figure 1b. In order to transform $J^T(t)$ into a curve which is simply related by a $\log a_T$ shift to $J^{T_0}(t)$ it is necessary to normalize it for these temperature induced changes in J_U and J_R . This is done by forming the normalized creep curve $J_p^T(t)^2$:

$$J_p^T(t) = \frac{1}{b_T} J^T(t) + J_U^{T_0} \left(1 - \frac{c_T}{b_T}\right) \quad (8)$$

this normalized curve is the broken curve in Figure 2b. The effect of the normalization is to shift the curve $J^T(t)$, at long times, in an upwards direction as indicated by vector (1) in Figure 2b: at short times the normalization moves the $J^T(t)$ curve downwards, as indicated by vector (2) in Figure 2b. The normalized curve $J_p^T(t)$ is related to the creep curve at $T_0, J^{T_0}(t)$:

$$J^{T_0}(t/a_T) = J_p^T(t) \quad (9)$$

Thus the shifting of $J_p^T(t)$ to the right along the time axis—plotted logarithmically—by $\log a_T$ will cause it to superpose exactly upon $J^{T_0}(t/a_T)$.

The effect of normalization is seen most easily at either of the edges of the relaxation where $J(t)$ is close to J_U or to J_R . Here the absence of normalization means the raw data can be seen not to fit when superposed horizontally. In the centre of the relaxation, where the creep curves have little curvature, the un-normalized curves can, apparently, be shifted by horizontal shifts onto the master-curve: however the value of $\log a_T$ so obtained is erroneous. The significance of the error involved depends on the magnitudes of the correction terms in equation (8), which we now assess.

For the α -relaxation of an amorphous polymer the ratio:

$$x = \frac{J_R^{T_0}}{J_U^{T_0}} \sim 10^3$$

This leads to an attractive simplification since^{2,13}

$$b_T = \frac{x d_T - c_T}{x - 1}$$

Both c_T and d_T are of order unity since the temperature coefficients of J_U and J_R produce changes below 1% per °C. So for $x \sim 10^3$, we have $xd_T \gg c_T$ and $x \gg 1$ so that

$$b_T \doteq d_T \tag{10}$$

There are two ways of obtaining d_T : either by assuming J_R is given by the theory of rubber elasticity and that the rubber is ideal: in which case^{1,2}:

$$d_T = \frac{\rho_0 T_0}{\rho T} \tag{11}$$

ρ_0 and ρ are the densities at T_0 and T . Or by an empirical method which we describe later. The reason for the use of an empirical method is that despite the elegance of the theory of rubber elasticity it holds only for an ideal rubber, one for which there is no change whatsoever in internal energy with deformation. For this reason we prefer to use the empirical procedure for obtaining d_T .

For the calculation of the order of magnitude of d_T . Equation (11) is sufficiently exact. Let the volume expansion coefficient be α , then for $(T - T_0) = \Delta T$

$$d_T = \frac{1 + \alpha \Delta T}{1 + \Delta T/T_0}$$

To gauge the magnitude of d_T take $\Delta T = 1$ K, $T_0 = 250$ K and $\alpha = 4 \times 10^{-4} \text{ K}^{-1}$, a reasonable value: then,

$$\begin{aligned} d_T &\doteq (1 - \frac{1}{250})(1 + 4 \times 10^{-4}) \\ &\doteq (1 - 0.4 \times 10^{-2})(1 + 0.04 \times 10^{-2}) \end{aligned}$$

It will be seen that the dominant term here is the first so that the second, the density term, can be neglected to within the usual experimental error. In which case we anticipate that at $T_0 \sim 250$ K for $\Delta T = 1$ K:

$$d_T = 1 - 0.4 \times 10^{-2}$$

The temperature coefficient d_T thus predicts a decrease in J_R at 250 K of 0.4% per 1 K increase in temperature. For ease of reference note that this is equal to approximately 10 x the coefficient of volume expansion.

The method of normalization using equation (8) is very elementary when $J^T(t) \gg J_U^T$. In which case we may neglect the second term on the right-hand side of equation (8) and from equations (8) and (9) write, after taking logs:

$$\log J^{T_0}(t/a_T) = \log J^T(t) - \log b_T \tag{12}$$

Thus the creep curves, when plotted $\log J^T(t)$ versus $\log t$, have to be shifted vertically by $(-\log b_T)$ before being shifted horizontally by $\log a_T$ to superpose onto the master curve. Note that if $(T - T_0)$ is positive $b_T < 1$, so that $(-\log b_T)$ is positive: in which case the $\log J^T(t)$ curve at T must be shifted upwards to obtain superposition, as indicated by vector (1) in Figure 2b. This method of normalization— $\log J(t)$ plotted against $\log t$ with vertical shift—can be used when $J(t) \gg J_U$, which in effect means, stating it in outline, the second and third decades of compliance rise (see Figure 5). The empirical method of obtaining $(-\log b_T)$ is based on the argument that only when the correct vertical shift has been applied

will the creep curves fit together with a horizontal shift. The ideal temperature change of J_R ($\sim 0.4\% \text{ K}^{-1}$) is however a useful quantity with which to gauge the empirically derived shift.

The normalization procedure is complex in the first decade of compliance rise. From equations (5) and (8):

$$J_p^T(t) = \frac{1}{b_T} [J^T(t) - J_U^T] + \frac{J_U^T}{c_T} \tag{13}$$

In general, to superpose in this region both b_T and c_T are required as well as J_U^T . However at the lowest temperatures, when the relaxation is just commencing, so that $J_U^T \gg (J^T(t) - J_U^T)$ it can be seen that the dominant coefficient will be c_T^{-1} . For $T > T_0$, $c_T > 1$ so that $c_T^{-1} < 1$. In which case it follows from equation (12) that the effect of normalization — for $T > T_0$ — is to move the creep curve downwards along the compliance axis as indicated by vector (2) in Figure 2b.

If data is not normalized before superposition the implicit assumption is that to within the error of the experiment:

$$b_T = c_T = d_T = 1$$

A method for testing this for shear creep data is described in the following Experimental section. An advantage of the dynamic technique used by Ferry and co-workers¹ is that if the superposition of $J'(\omega)$ and $J''(\omega)$ is found to generate different shift factors, then normalization of one or both is required. Or again, if the data is incorrectly normalized, $J'(\omega)$ and $J''(\omega)$ will generate different and therefore worthless shift factors. This automatic fail-safe method in the dynamic experiment is not available in creep, so it is necessary to exercise considerable caution: the way in which this caution can be exercised is described in the results section (note Table 1).

Thermal sampling

The technique has been described elsewhere^{9,14}. Note that in the theory of the TS experiment it is not necessary that all relaxation times within the extremely wide distribution have the same activation energy, i.e. have the same shift factor. What is required is that the narrow packet of relaxation elements stimulated—of order 1 to 2 decades wide—should have the same shift factor to within the error of the experiment⁹. In $t-T$ superposition as applied to creep, the requirement of constant shift factor is much more stringent: it applies to all the elements contributing effectively to one creep curve, which means in fact an extremely wide band, one of order eight decades wide. The two methods, TS and $t-T$ superposition, are thus equally valid for a relaxation in which the whole relaxation distribution moves with constant shift factor: if the compensation rule applies, $t-T$ superposition fails but TS is still valid.

EXPERIMENTAL

The copolymer selected was Krynac 806 stated to have a bound acrylonitrile content of 50%. It was compounded as follows: Krynac 806, 100 parts: stearic acid, 1 part: zinc oxide, 4 parts: antioxidant (Permanex BL), 1 part: sulphur, 1.5 parts: accelerators, CBS 0.8 parts and TMTD, 0.2 parts. After compounding it was cured as a

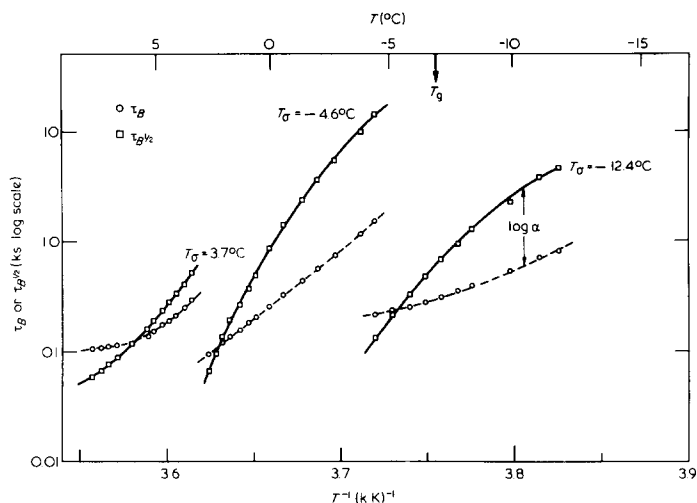


Figure 3 Circled points show the BFG plot of $\log \tau_B$ versus T^{-1} for three TS experiments. The squared points show the data corrected by the McCrum procedure plotted $\log \tau_{B\frac{1}{2}}$ versus T^{-1}

sheet 1 mm thick at 150°C for 30 min. The glass transition was observed at $T_g = -7.0^\circ\text{C} \pm 1^\circ\text{C}$ at a cooling rate of $10^\circ\text{C min}^{-1}$; the measurement was by differential scanning calorimetry (d.s.c.).

A specimen of length 50 mm and breadth 10 mm was cut from the sheet and mounted in a torsional creep apparatus with temperature control based on the method of Schwippert and van der Waal¹⁵. In this system liquid nitrogen is evaporated to produce a stream of cold, dry gaseous nitrogen which is passed over a controlled heater and so brought to the required temperature: it then passes over the specimen and from thence exhausted to the atmosphere. One of the several advantages of this elegant system is the fact that moisture is eliminated by the flow of dry nitrogen gas. Although NBR rubber is stated to have extremely low affinity for water, it was decidedly advantageous to be able to eliminate its effect in this way without a vacuum system.

In the TS experiment the specimen was maintained at 20°C for 20 min and then cooled at 1°C per min to the stressing temperature, T_σ . TS experiments were performed at six stressing temperatures between -15°C and $+3.7^\circ\text{C}$. A σ -run and an α -run (the nomenclature of ref. 9) were performed in succession at each stressing temperature: no z-run was required since the temperature induced zero shift was negligible. In the σ -run the specimen was aged for a time $t_a = 120$ min at T_σ : a constant torsional stress was then switched on, and switched off 6 min later. The specimen was left at T_σ to recover for a further 1 min and was then quenched to 30°C below T_σ . The heating run was then initiated at a heating rate of 2°/min, during which the time dependence of the recovering strain $\gamma(t)$ was recorded on a graphispot: differentiation of $\gamma(t)$ yielded $\dot{\gamma}(t)$. The specimen after reaching 20°C was stored at that temperature for 30 min. The α -run was then initiated: the specimen was cooled to T_σ at 1°C/min: it was aged at T_σ for $t_a = 120$ min, as in the σ -run. A stress was then switched on, again for $t_\sigma = 6$ min and the recovery observed isothermally at T_σ for a considerable time to obtain the correction factor α , as described elsewhere⁹.

In the shear creep experiments the specimen, after overnight storage at room temperature, was heated to 30°C and stored at that temperature for 10 min. It was then cooled at 2°/min to the stressing temperature:

experiments were performed at ten stressing temperatures between -19.8°C and $+8.5^\circ\text{C}$. The ageing time at the stressing temperatures was $t_a = 240$ min. The stress was then switched on and creep measurements made for 10^3 s. The specimen was then heated to room temperature and stored overnight before the next experiment. All measurements were made in the linear region at strains below $\gamma = 10^{-3}$.

RESULTS

TS experiments

Values of $\log \tau_B^T$ for three of the six TS experiments:

$$\tau_B^T = \frac{\gamma^T}{\dot{\gamma}^T} \tag{14}$$

are plotted (open circles, broken lines) in Figure 3 against T^{-1} in a BFG plot: the other three experimental results are plotted similarly in Figure 4. The BFG plot for a polymer with a distribution of relaxation times is of unquantifiable significance⁹. It is however possible to calculate a relaxation time of direct physical significance, $\tau_{B\frac{1}{2}}^T$. The temperature dependence of $\tau_{B\frac{1}{2}}^T$ is representative of the temperature dependence of the packet of relaxation times stimulated in the experiment. The McCrum correction factor α was calculated by Method 2 of ref. 9 and was used to obtain $\tau_{B\frac{1}{2}}^T$ from the observed values of τ_B :

$$\tau_{B\frac{1}{2}}^T = \alpha \tau_B^T \tag{15}$$

Values of $\log \tau_{B\frac{1}{2}}^T$ are plotted against T^{-1} (squared points, solid lines) in Figures 3 and 4. It will be seen that the plot of $\log \tau_{B\frac{1}{2}}^T$ versus T^{-1} is curved in all six experiments. This is in marked distinction to the observations at the α and β relaxations in crystalline polypropylene where the plots of $\log \tau_{B\frac{1}{2}}^T$ against T^{-1} in all cases fit the compensation rule¹⁴.

It can be stated at once that the data shown in Figures 3 and 4 do not support the findings of Zielinski *et al.*⁵ and of Lacabanne *et al.*⁴ that the kinetics of the α -relaxation of amorphous polymers follow the compensation rule. Note that the BFG plot ($\log \tau_B^T$ against T^{-1}) yields curves which are systematically concave up: this curvature is typical of

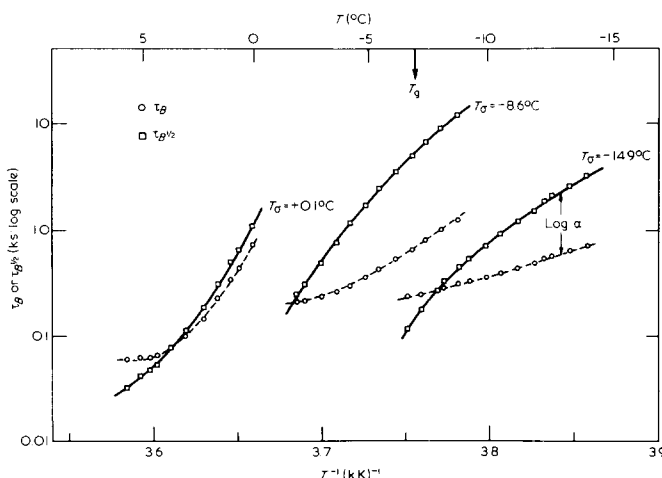


Figure 4 Circled points show the BFG plot of $\log \tau_B$ versus T^{-1} for three TS experiments. The squared points show the data corrected by the McCrum procedure plotted $\log \tau_{B\frac{1}{2}}$ versus T^{-1}

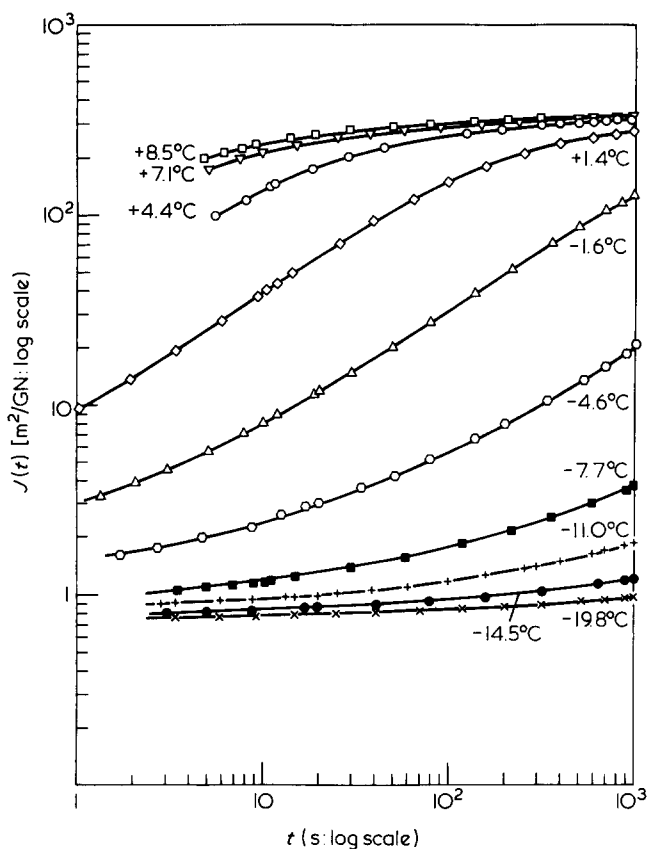


Figure 5 Dependence of the creep compliance $J(t)$ on time (plotted on a double-logarithmic scale) for an NBR elastomer at temperatures between -19.8°C and $+8.5^{\circ}\text{C}$. Prior to each creep experiment the specimen was cooled from 30°C to the stressing temperatures at 2°C per minute and was equilibrated for four hours before the stress was applied. The data contains an ageing perturbation below -4.6°C : the T_g of the specimen was -7.0°C

the BFG plot and does not depend on the polymer or on the relaxation mechanism. The McCrum plot ($\log \tau_{B\frac{1}{2}}^T$ versus T^{-1}) shows a curvature which changes completely with the stressing temperature T_{σ} , Figures 3 and 4, being concave down at the lowest temperatures and concave up at the highest. The significance of these results is outlined in the Discussion section.

Shear creep

The compliance, $J(t)$, observed at temperatures between -19.8°C and $+8.5^{\circ}\text{C}$ is plotted $\log J(t)$ against $\log t$ in Figure 5. Time-temperature analysis was attempted without normalization: the curves were shifted horizontally along the $\log t$ axis. Superposition was not possible at most temperatures: the curves usually did not fit together. The extent of the misfit can be gauged from Table 1 which shows the separations at three points along the curves. For instance the separation, $\Delta \log a_T$, between the two creep curves at -19.8°C and -14.5°C is 1.20 at short times, 0.96 at intermediate times and 0.72 at long times. The change in separation between the curves at the highest temperature is in the same sense: thus between the $+7.1^{\circ}\text{C}$ and $+8.5^{\circ}\text{C}$ curves the separation varies from 0.17 at short times to 0.13 and thence to 0.08 at long times. In the centre of the relaxation, between the pairs of curves (-4.6°C , -1.6°C), (-1.6°C , $+1.4^{\circ}\text{C}$), ($+1.4^{\circ}\text{C}$, $+4.4^{\circ}\text{C}$) the values of $\Delta \log a_T$ are constant: the creep curves are parallel. The significance of the derived values of $\Delta \log a_T$ for these curves is taken up in the Discussion section.

Whilst the specimen was equilibrating before the commencement of the 10^3 s creep experiment, short time creep experiments were performed to test for the presence of physical ageing¹⁶. Physical ageing was not detected after 4 h equilibration at temperatures above -4.6°C : below -4.6°C physical ageing was observed. The shift-factors observed below -4.6°C are therefore perturbed by ageing. The value of $t-T$ superposition under this circumstance depends on the theory of the ageing mechanism, an exceedingly complicated topic, to which we return in the Discussion.

DISCUSSION

Before examining the implication of the TS results, Figures 3 and 4, we consider the evidence from the shear creep experiment. Following Schwarzl and Zahradnik¹¹ we take as a convenient, but arbitrary, reference temperature one in the centre of the relaxation: this is the temperature at which the creep compliance at 16 s equals approximately the mid-point between J_U and J_R , and we denote it T_s . For this NBR polymer we find $T_s = -1^{\circ}\text{C}$ (6°C above T_g). In Figure 6 $\log a_T$ is plotted against $(T - T_s)$. The circled points are values of $\log a_T$ taken without vertical shift: in temperature regions where adjacent creep curves were not parallel $\Delta \log a_T$ was estimated at the point where the curves crossed in the centre of their span.

Another set of shift-factors was obtained using a vertical shift. In the top two decades of compliance rise this vertical shift is $(-\log b_T)$: this quantity was obtained by using the principle of optimum-fit. The curves were moved vertically by $(-\log b_T)$ and then moved horizontally to yield $\log a_T$: one unique combination of a small vertical shift and a considerably larger horizontal shift will optimize fit. The values of $\log a_T$ so obtained are plotted in Figure 6 as open squared points (zone a-b). The closed squared points represent data obtained in the central temperature region (-4.6°C to $+4.4^{\circ}\text{C}$) where no vertical shift was required to obtain fit (zone b-c). At lower temperatures the optimum-shift method was used also to obtain values of $\log a_T$: these values are given by the open squares in Figure 6 (zone c-d). All the data points in zone

Table 1 Three readings of the logarithm of the shift factor between adjacent compliance curves, $\Delta \log a_T$: the first is at short times and the third at long times, and the second in between. In the centre of the relaxation, over the interval -4.6°C to $+4.4^{\circ}\text{C}$, the shift factor between adjacent curves is constant: the curves are parallel. But outside this central band, at higher and lower temperatures, the shift factor between adjacent curves is not a constant: it diminishes at longer times. Superposition cannot therefore be achieved outside the central band without a vertical shift. The direction of this shift — up at high temperatures and down at low temperatures — is in accord with theory

T_{σ}	First	Second	Third
$+8.5^{\circ}\text{C}$	0.17	0.13	0.08
$+7.1^{\circ}\text{C}$	0.58	0.49	0.40
$+4.4^{\circ}\text{C}$	0.89	0.91	0.92
$+1.4^{\circ}\text{C}$	1.13	1.15	1.14
-1.6°C	1.31	1.33	1.30
-4.6°C	1.60	1.48	1.40
-7.7°C	1.07	1.02	0.91
-11.0°C	1.20	1.06	0.96
-14.5°C	1.20	0.96	0.72
-19.8°C			

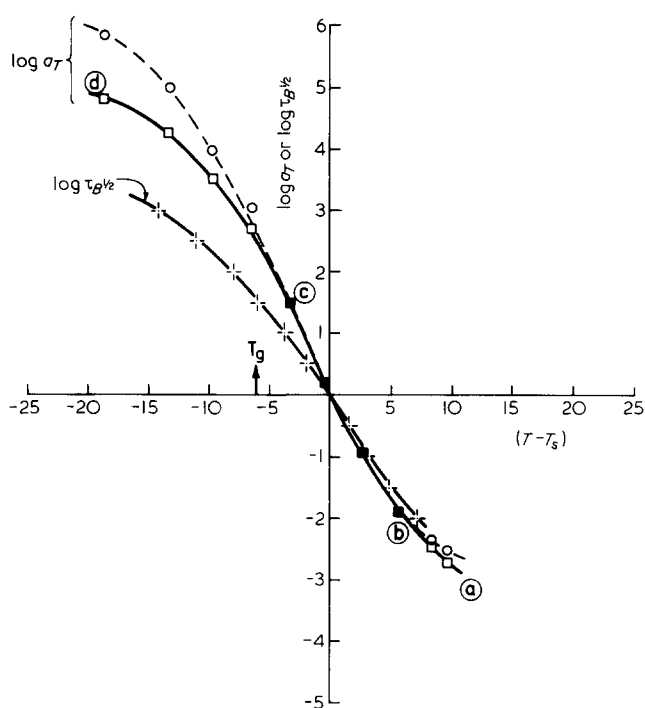


Figure 6 Shift factor $\log a_T$ plotted against $(T - T_g)$ with reference temperature $T_g = -1.0^\circ\text{C}$. The circled points show values of $\log a_T$ taken without any vertical shift: the squared points show $\log a_T$ taken with the optimum vertical shift: the filled squared points show $\log a_T$ taken in regions where no vertical shift is required for optimum fit. The method of $t-T$ superposition is most reliable in this zone, labelled b-c: it is less reliable in zone a-b because the optimum vertical fit is not easy to determine: $t-T$ superposition is of no value in zone c-d because the normalization is difficult to achieve (see equation (8)) and also because of perturbations due to physical ageing. Also shown is a plot of $\log \tau_{B1/2}$ — obtained by superposition as described in text — against $(T - T_g)$

c-d lay below T_g . Note that in this region the use of a vertical shift is not so theoretically understandable as in zone a-b: there are the additional problems in zone c-d due to physical ageing, to which we return later.

The reader will recall that theory predicts the direction of vertical shift between a pair of adjacent curves to be for the creep curve at the higher temperature to move:

- (i) upwards at temperatures high in the relaxation region;
- (ii) downwards at temperatures low in the relaxation region.

This was in fact observed. The magnitudes of the optimum vertical shifts were very small, of order 1% per $^\circ\text{C}$. But because of the curvature of the creep curves this small vertical movement had a pronounced effect on the fitting of the curves in zones a-b and c-d, of Figure 6 and on the derived values of $\log a_T$.

In the central band (-4.6°C to $+4.4^\circ\text{C}$ Figure 5, zone b-c Figure 6), where no vertical shift was required for optimum fit, we examined the effect of a vertical shift of order 1% per $^\circ\text{C}$ on the observed $\Delta \log a_T$. It is rational to assume that in this region a vertical shift is strictly required ($-\log b_T$, equation (12)) and that the value of the shift is the same as in the top band, where shifts are quite obviously required for fit. That the eye cannot detect the need for a shift in the central band does not mean that a shift is not required for a precise analysis. We have found however, that vertical shifts of the order expected—1%

per $^\circ\text{C}$ —make a negligible difference to the values of $\Delta \log a_T$. In which case we can state that in the central zone (b-c, Figure 6) the values of $\Delta \log a_T$ are reliable to within the random error of the experiment: there is no systematic error of consequence.

Values of shift factors obtained by optimum fit in zone a-b, Figure 6, are less reliable since the method of shifting the curves vertically and horizontally is somewhat subjective. Nevertheless the values of $\log a_T$ obtained in the zone a-b by optimum fit (open squares, Figure 6) are certainly more reliable than the values taken without vertical shift (zone a-b, open circles, Figure 6). The latter data has a limited use in that it yields an upper limit to the $\log a_T$ versus $(T - T_g)$ curve at high temperatures.

It will be noted that we find reliable the temperature dependence of $\log a_T$ (see Figure 6) from 3°C above T_g to 11°C above T_g , a short span of temperature. For this reason there is no great purpose in checking the data against the WLF equation. In any case, the WLF equation is more reliably tested by the high frequency procedures—such as those of Ferry and co-workers¹—which can be tested by the superposition of a pair of coupled parameters, J' and J'' , or E' and E'' .

We turn now to the problem of physical ageing in the low temperature zone near the glass transition, discussed earlier by Schwarzl and Zahradnik¹¹. The validity of $t-T$ superposition in this region—when ageing is present—is at present in dispute. Early work in poly(vinyl acetate) and poly-n-butyl methacrylate showed the spectrum to change shape^{1,17}: equation (7) will not hold in this case and the use of $t-T$ superposition is precluded. The superposition technique has been used, however, by Struik¹⁶ as part of a wide fronted attack on the mechanisms of ageing. Other work on poly(methyl methacrylate) due to Read¹⁸ has supported the earlier conclusion that below T_g the spectrum changes shape. The spectrum also changes shape in polypropylene^{19,14}: this is a crystalline polymer so this fact may not be relevant in this context.

Only if the spectrum does *not* change shape can a shift factor, a_e , be defined to describe its movement to longer times as the ageing (or elapsed) time-after-cooling increases²⁰. Parameters b_e, c_e may be defined to describe the elapsed-time dependence of $(J_R - J_U)$ and J_U ²⁰. In which case a rigorous formalism for superposition can be developed. But, the experimental validity of this procedure has yet to be established. We take the view therefore, that the shift-factors taken below -4.6°C (zone c-d, Figure 6) in the temperature region where ageing effects were observed, are without physical significance due to spectrum shape change. This data is also undoubtedly perturbed by temperature dependence of the limiting compliances.

It is one of the advantages of the TS technique that ageing is not a significant perturbation. We turn accordingly to examine the six results for the temperature dependence of $\log \tau_{B1/2}$, obtained in the six TS runs shown in Figures 3 and 4. It will be recalled that a $\log a_T$ versus $(T - T_g)$ plot with reference temperature T_g , such as Figure 6, yields the temperature dependence of a representative relaxation time which equals 1 second at T_g . Now this information, the temperature dependence of a representative relaxation time, can be obtained by plotting $\log \tau_{B1/2}$ against T , or against T^{-1} as in Figures 3 and 4. From these graphs, it can be seen at once that the outline evidence

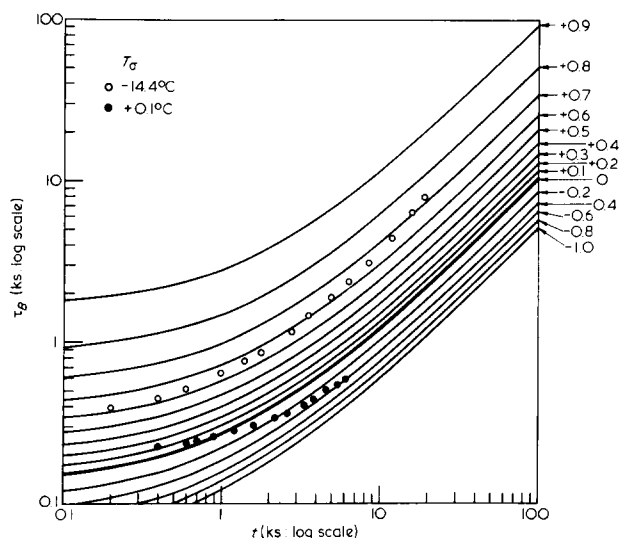


Figure 7 Comparison of a Voigt model theory (lines) against experiment (points) for an α -experiment in which $t=360$ s, $t_d=60$ s; q , the ramp slope, takes the value shown on the right. Open circles, data taken at -14.4°C ; closed circles, data taken at $+0.1^\circ\text{C}$

from t - T superposition is reproduced. At the lowest temperatures the form of the temperature dependence is curved, in a manner which shows the relaxation times to decrease at an ever increasing rate as the temperature rises. At the highest temperatures there is still curvature but in the opposite sense: the relaxation times continue to decrease with rising temperature but the rate of decrease gets lower and lower as the temperature rises.

In principle, the plots of $\log \tau_{B\frac{1}{2}}$ against T^{-1} —or against T —should superpose with a vertical shift: the reason is as follows. According to the TS theory the experimental stress history stimulates a packet of relaxation times, one of which is labelled $\tau_{B\frac{1}{2}}$, and its movement with change in temperature is monitored in the experiment⁹. Each of the six TS experiments shown in Figures 3 and 4—with the same values of t_σ and t_d but with different T_σ —stimulates a different $\tau_{B\frac{1}{2}}$. For instance the experiment with a T_σ of -12.4°C , Figure 3, yielded on the heating run a $\tau_{B\frac{1}{2}}$ at -10°C of 2.6 ks which decreased to 0.1 ks at -4°C ; at the same temperature, -4°C , the experiment with a T_σ of -4.6°C (Figure 3) yielded at $\tau_{B\frac{1}{2}}$ of 12 ks. Now at -4°C the slope of the $\log \tau_{B\frac{1}{2}}$ versus T^{-1} plot should be the same in the two experiments if a_T is dependent only on temperature. It should therefore be possible to move the $\tau_{B\frac{1}{2}}$ curves of Figures 3 and 4 vertically to yield a master curve. This has been done with fair success: that is to say the overall direction of slope is reproduced but the fit is not perfect: we return to explain this point later. The resulting master curve labelled $\log \tau_{B\frac{1}{2}}$ is plotted in Figure 6 for comparison with the $\log a_T$ value derived from the shear creep studies. It will be noted that a sigmoid curve results in outline form comparable to results from shear creep, but different in detail.

In the low-temperature glassy region, zone c-d, Figure 6, the TS data is the more reliable. The data from t - T superposition is largely without value on the two counts mentioned above: that is to say, lack of a correct normalization procedure and the unknown physical ageing perturbation.

In region b-c both sets of data are reliable: they disagree because in this region the quantity of significance is the volume. In this temperature region the volume

attained depends on the experimental thermal prehistory. In the creep experiment the volume is probably close to its equilibrium having been slow cooled to the measuring temperature and equilibrated for 4 h. In the TS experiment the data was taken with a heating rate of $2^\circ/\text{min}$. It is most unlikely that in the TS experiments on the heating run the volumes were in equilibrium: nor is it likely that in any pair of TS experiments that on the heating run at one particular temperature the volumes were the same. This explains satisfactorily the fact that the TS data do not *in detail* fit together with a vertical shift: they do fit together in general outline. An appropriate way to perform experiments in this region is to measure the volume simultaneously¹¹ on the heating run. In this way the predictions of the WLF equation could be studied with precision using the TS technique.

We now examine the reason for the systematic change in the correction factor α . The $\log \tau_B$ versus T^{-1} plot is curved, always concave up. The $\log \tau_{B\frac{1}{2}}$ versus $1/T$ plot is curved, concave up at the highest temperatures but concave down at the lowest. From equation (15), note that since:

$$\log \alpha = \log \tau_{B\frac{1}{2}} - \log \tau_B \quad (16)$$

the vertical separation in Figures 3 and 4 between $\log \tau_B$ and $\log \tau_{B\frac{1}{2}}$ lines equals $\log \alpha$. For example in Figure 4 the maximum $\log \alpha$ values are large for the $T_\sigma = -14.9^\circ\text{C}$ experiment taking values up to $\log(3.7/0.77) = 0.74$: for the $T_\sigma = +0.1^\circ\text{C}$ experiment the largest value is $\log(1.4/0.9) = 0.19$. This is entirely due to the change in the slope of the distribution function.

If the distribution is a ramp of constant slope q (ref. 14, equation (10)), and if $t_\sigma = 6$ min and $t_d = 1$ min, then the value of τ_B observed in the isothermal α experiment at time t is given by the lines shown in Figure 7 (compare ref. 14, Figure 5). Data from two α -runs, those at -14.4°C and $+0.1^\circ\text{C}$, is plotted in Figure 6. At -14.4°C the points show that the ramp is not of constant slope—which is hardly to be expected—but that it is positive and at low t close to $q = 0.5$ and at high t (~ 20 ks) close to $q = 0.7$. Thus at -14.4°C (-7.4°C below T_g) the slope of the distribution is increasing with $\log t$: qualitative reference to Figure 5 and the creep curve at -14.5°C confirms this observation. On the other hand—see Figure 7—at $+0.1^\circ\text{C}$ the data show a small but positive ramp at times below 1.0 ks and a negative ramp about 1 ks, so that in this time scale the distribution maximum occurs at $+0.1^\circ\text{C}$. Again, referring to Figure 4 it will be seen that the creep curves taken closest to $+0.1^\circ\text{C}$ (at -1.6°C and $+1.4^\circ\text{C}$) confirm qualitatively this point. The large change in the correction factor α , caused by changes in magnitude and sign of the ramp slope q , is the origin of the startling change in concave down to concave up curvature of the $\tau_{B\frac{1}{2}}$ plots in Figures 3 and 4 as the temperature increases from below to above T_g .

It will be clear therefore that for a relaxation with such a sharply peaked distribution of relaxation times the correction factor α is extremely important. It is of decreasing importance for negative q , since in this case the absence of long relaxation times causes the stimulated packet to narrow, so that it conforms more closely to the packet that would have been stimulated in a single relaxation time model (compare Figure 10 of ref. 14). As evidence of this, note the similarity between the $\log \tau_{B\frac{1}{2}}$

and $\log \tau_B$ versus T^{-1} plots for the two TS experiments at the highest temperatures $T_g = +0.1^\circ\text{C}$ (Figure 4) and $T_g = +3.7^\circ\text{C}$ (Figure 3).

The difference between the earlier TS experiments^{4,5} and the results reported here must lie in the neglected part of the recorded data. The earlier workers plotted only the data at lower temperatures which conforms, more or less, to an Arrhenius plot. It will be seen from Figures 3 and 4 that by eliminating in each $\log \tau_B$ versus T^{-1} plot 50% of the data, that at the highest temperatures, the resulting Arrhenius plots have only a slight curvature and that the overall result shows a series of slopes which increase with T_g .

Finally, comparing the two techniques, TS and t - T superposition, it can be stated that in the central temperature band where the conclusions are insensitive to vertical shifts, the t - T superposition method is the more reliable. It is not reliable outside this band: at high temperatures because it is difficult to obtain the correct vertical shift and at low temperatures for the same reason, compounded by the physical ageing perturbation. TS is valuable particularly in this low temperature region. It is in precisely this circumstance—low creep rates, physical ageing—that TS spectroscopy has particular potential.

FUTURE EXPERIMENTS

A most useful guide to future study of the kinetics of α -relaxation processes for $T < T_g + 10^\circ\text{C}$ is the hybrid equation of Kovacs, Hutchinson and Aklonis²¹. The temperature and structure dependence of the i th process is given by:

$$\tau^i = A \exp \left[\frac{\Delta H^i}{RT} + \frac{b}{f_T} \right] \quad (17)$$

in which ΔH^i is the activation enthalpy of the i th process and

$$f_T = f_g + \Delta\alpha(T - T_g) \quad (18)$$

For $T < T_g$ it is presumed the structure does not change, so that f_g is the frozen-in free volume. In which case at temperatures T and T_0 below T_g :

$$\ln a_T = \ln \frac{\tau^i}{\tau_0^i} = \frac{\Delta H^i}{R} \left[\frac{1}{T} - \frac{1}{T_0} \right] \quad (19)$$

For temperatures T and T_0 above T_g :

$$\ln a_T = \frac{\Delta H^i}{R} \left[\frac{1}{T} - \frac{1}{T_0} \right] + b \left[\frac{1}{f_T} - \frac{1}{f_{T_0}} \right] \quad (20)$$

For this circumstance T affects $\ln a_T$ directly through the first term on the right-hand side and indirectly through its control of structure, as represented by the free-volume f_T in the second term²¹. The questions to be answered are as follows:

(1) Is ΔH^i a constant for all relaxation processes, or does the compensation rule hold? This can only be answered by TS experiments at temperatures well below T_g : in our experiments the lowest T_g was -14.9°C , only 8°C below T_g . It is clear from Figure 4 that the $\log \tau_{B\lambda}$ run for this experiment showed a curvature which is best explained (in the absence of additional information) by postulating that the heating run was accompanied by structural changes as T increased. The TS experiments

must therefore be performed at lower temperatures. Zielinski *et al.*⁵ and Lacabanne *et al.*⁴ have already performed such experiments, which if corrected by determining $\tau_{B\lambda}$, could well resolve this point. The results of Read¹⁸ in PMMA provide strong evidence that ΔH^i is not a constant, but that it increases systematically as τ^i increases.

(2) Above T_g it must be shown that the first term on the right-hand side of equation (20) is negligible with respect to the second.

CONCLUSION

Earlier reports that TS shows the compensation rule to hold at temperatures below the glass transition of an amorphous polymer are rejected. TS experiments on a copolymer of acrylonitrile and butadiene, corrected by the method of McCrum, show the compensation rule not to hold at temperatures between ($T_g - 8^\circ\text{C}$) and ($T_g + 17^\circ\text{C}$). The early TS experiments, if corrected, could test the applicability of the compensation rule at temperatures below ($T_g - 8^\circ\text{C}$). Step-function experiments analysed by t - T superposition are reliable in the short temperature range from ($T_g + 3^\circ\text{C}$) to ($T_g + 11^\circ\text{C}$). At temperatures above ($T_g + 11^\circ\text{C}$), t - T superposition is reliable if an appropriate b_T normalization is applied. At temperatures below ($T_g + 3^\circ\text{C}$) the method fails operationally through lack of appropriate normalization and also because of ageing perturbation.

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