Mechanism of physical aging in crystalline polymers

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The mechanism of physical aging in isotactic polypropylene was studied in the α-region (15–80°C) by thermally stimulated creep and by creep superposition. Aging for an elapsed time t_e was observed to have no effect on retardation elements at τ for $\tau \gg t_e$. Thus the pronounced effects observed in aging cannot be due to the movement of the retardation spectrum as a whole to longer times. The method of time-elapsed time $(t-t_e)$ superposition fails because the retardation spectrum changes shape. This change in shape leads to systematic deficiencies in the superposed curves, an effect which shows up most clearly in superposition of the differentiated creep curves. The possible changes that take place during aging are a change in magnitude of the retardation elements and a shift to longer times. These changes will only occur in retardation elements at τ when $\tau \lesssim t_e$.

INTRODUCTION

We describe a study of the conclusions of Struik[1,2] concerning the mechanism of physical aging in crystalline polymers. In polypropylene Struik observed that, after a quench from 120 to 20°C, large reductions in compliance occurred whilst the specimen was stored at 20°C. The effect is accompanied by a decrease in specific volume. The impact of Struik's work stems firstly, from the systematic experimental attack on an old, but unsolved problem of technological and philosophical interest. Secondly, from the primary hypothesis that the large compliance changes are due to an iso-thermal shift of the distribution of retardation times; a shift to longer times of approximately one decade for each ten-fold increase in elapsed time, t_e.

For polymeric liquids above the glass transition temperature, it is accepted that the distribution of mechanical retardation times is shifted by a change in temperature through the temperature induced change in free-volume. Following Ferry[3], if v is the specific volume and v_f that portion of v which is free-volume, then when the temperature is changed, each retardation time τ_0 at T_0 becomes $\tau = a_T\tau_0$ at T and, the shift-factor a_T is given.

$$\ln a_T = B\left[\frac{1}{f(T)} - \frac{1}{f(T_0)}\right] \tag{1}$$

in which $f = (v_f/v)$ at T_0 or T and B is a constant. This equation has been successful in coordinating a vast amount of experimental data from both mechanical and dielectric experiments at temperatures above T_g. In this range the shifting of appropriately normalized experimental parameters leads to a determination of a_T. For example both real $J'(\omega)$ and imaginary $J''(\omega)$, components of the shear compliance, shift by the same amount. Equation 1 is extremely well tested for polymeric liquids and the derived a_T really does record the shift of the spectrum which is uniquely determined by free-volume.

There is a major difference, however, between this circumstance and that existing above 0°C (region of α-relaxation process) in partially crystalline polypropylene. In this temperature range the volume of polypropylene and hence the free-volume exhibit a well defined time dependence after any change in temperature[2], a phenomenon known also in polyethylene[4]. Whereas for polymeric liquids in the range of applicability of equation 1 the volume and free-volume are always in equilibrium and show no time dependence. The relaxation times governing volume recovery above T_g are so short that it is impossible to change the temperature fast enough to obtain a volume other than the equilibrium volume.

The problem of the time dependent free-volume was tackled by Kovacs, Stratton and Ferry[5] and by Meyer, Mangin and Ferry[6] for amorphous polymers at temperatures just below T_g. Suppose the specimen is in volume equilibrium at T_0 (close to T_g) with equilibrium fractional free-volume $f(T_0, \infty)$. Let it be quenched to T and after an elapsed time t_e the instantaneous fractional free-volume is $f(T, t_e)$. The instantaneous shift factor is then

$$\ln a_{T,t_e} = B\left[\frac{1}{f(T,t_e)} - \frac{1}{f(T_0,\infty)}\right] \tag{2}$$

Whereas equation 1 is fully accepted, equation 2 remains to be established quantitatively. For instance, it was observed that in polyvinyl acetate and in poly-n-butyl methacrylate the retardation spectrum in the glassy state changed shape[3,5,6] in a manner which should preclude the precise use of time-temperature equivalence, a fact which questions the definition of the shift-factor. Furthermore Struik[1] has shown that free-volume models are not self-consistent when applied quantitatively to physical aging.

The Struik model, although lacking a mechanistic, theoretical background, is extremely challenging. Its premiss is of the greatest significance. We have therefore examined it in some detail to determine whether or not physical

aging is produced by shifts of the entire spectrum. Firstly, by the use of thermally stimulated creep recovery to determine directly whether or not long relaxation times are shifted during aging. Secondly, by superposition experiments which follow the rational and efficient pattern pioneered by Struik, but in which greater discrimination is achieved in analysis by examining differentiated creep curves.

THEORY OF SUPERPOSITION

Some years ago we observed a marked diminution in relaxation magnitude which was produced by thermal aging[7-9]. in the γ and β regions of linear polyethylene. A specimen of linear polyethylene was quenched from room temperature to liquid nitrogen temperature. It was then heated into the the γ-region at a rate $1°C$ min^{-1} with simultaneous observation at 0.67 Hz of logarithmic decrement and shear modulus. The results were compared with a specimen which had been cooled very slowly from $20°C$. No shift of the position of the γ_I peak was observed. Large changes in logarithmic decrement and shear modulus were observed however, which were clearly attributable to changes in relaxation magnitude. A quenched specimen exhibits a relaxation magnitude higher than a specimen which is thermally equilibrated. Indeed the β-relaxation in linear polyethylene is so small that it is observable only when magnified by quenching. In a thermally equilibrated specimen the β-relaxation cannot be distinguished from the background, an effect also observed in polyoxymethylene[10]. This phenomenon is not due to changes in crystalline volume fraction but is a manifestion of physical aging. In formulating a linear viscoelastic theory of elapsed time dependence we shall therefore start with the most general *a priori* assumption that after the quench increasing t_e affects J_U and J_R (the limiting compliances) as well as the temporal position of the retardation spectrum. More restrictive assumptions will be introduced later whose effects can be gauged from the resulting closed form expression (equation 6).

We require to model an experiment in which the specimen is first heated until it attains a state of pseudo equilibrium at temperature T_2 and is then quenched to a lower temperature T_1. The specimen is maintained isothermally at T_1. The viscoelastic parameters change with increasing elapsed time, t_e. Let the t_e dependencies of the limiting compliances at T_1 be given by the parameters b_e and c_e.

$$J_R^e - J_U^e = b_e(J_R^{eo} - J_U^{eo}) \tag{3}$$

$$J_U^e = c_e J_U^{eo} \tag{4}$$

J_R^e and J_R^{eo} are the relaxed compliances at elapsed time t_e and the reference elapsed time t_e^0 with similar notation for the unrelaxed complainces J_U^e and J_U^{eo}. Assume that with increasing t_e the distribution of retardation times shifts uniformly along the $\ell n\tau$ axis without change in shape and also changes uniformly in magnitude,

$$L^e(\ell n\tau) = b_e L^{eo}(\ell n[\tau/a_e]) \tag{5}$$

This assumption for the case of $t-T$ equivalence is due originally to Alfrey[11]. Its use here for $t-t_e$ equivalence is a statement of the Struik hypothesis. The purpose of the paper is to examine the validity of Equation 5.

From linear viscoelastic theory[12,13] it follows that

$$J^{eo}(t/a_e) = \frac{1}{b_e} J^e(t) + J_u^{eo} \left[1 - \frac{c_e}{b_e} \right] \tag{6}$$

The implication of this equation for graphical superposition depends on whether the superposition is performed using data plotted $J^e(t)$ versus log t or log $J^e(t)$ versus log t, and whether or not, in addition to the horizontal shift along the time axis, a vertical shift is applied. There are four methods of superposition to consider, all employed by Struik[1].

If the data to be superposed is plotted $J^e(t)$ versus log t, with or without vertical shift, the premiss is that $b_e = 1$. It may therefore be stated, with regard to equation 6, that superposition of $J^e(t)$ by horizontal shift alone assumes:

Method 1: $a_e \neq 1$; $b_e = c_e = 1$

And by horizontal and vertical shift of $J^e(t)$:

Method 2: $a_e \neq 1$; $b_e = 1; c_e \neq 1$

It also follows from equation 6 that superposition of log $J^e(t)$ by horizontal shift alone assumes:

Method 3: $a_e \neq 1$; $b_e = c_e = 1$

And by horizontal and vertical shift of log $J^e(t)$:

Method 4: $a_e \neq 1$; $b_e = c_e \neq 1$

In all four methods the horizontal shift is $-\log a_e$: in Method 2 the vertical shift is $J_u^{eo}[1 - c_e]$ and in Method 4 the vertical shift is $-\log b_e$.

The superposition procedure is susceptible to extremely small departures of b_e and c_e from unity which can lead to gross errors in the observed a_e. This is particularly so when the slope of $J^e(t)$ with respect to log t is small as discussed elsewhere[12,14,15]. This is the case in polypropylene, in which we shall be interested in creep at temperature low in the α-region. The problem is that neither b_e nor c_e is known and that these parameters have to be determined in the analysis in addition to a_e.

In Methods 1 and 2 it is assumed that $b_e = 1$; the relaxation magnitude is taken not to change with increasing t_e. This drastic assumption is not based on physical argument but on operational convenience. The data when plotted $J^e(t)$ versus log t may be manipulated by moving one graph over another either horizontally, or horizontally and vertically. If the assumption $b_e = 1$ is rejected the analysis becomes most formidable in that the effect of b_e^{-1} in the first term of equation 6 is to move the $J^e(t)$ curve vertically but also to induce a change in slope. Additionally there is another vertical shift (last term of equation 6) which involves both b_e^{-1}, c_e and J_U^{eo}. With such a multiplicity of parameters a penetrating analysis by graphical superposition using Methods 1 and 2 is impossible. Method 4 is the only operational procedure available for the assumption $b_e \neq 1$ but then its use is limited by the additional restriction $b_e = c_e$.

It is possible however to eliminate one of the parameters by differentiating equation 6 which after taking logs, yields

$$\log \dot{J}^{eo}(t/a_e) = \log \dot{J}^e(t) + \log a_e - \log b_e \tag{7}$$

According to this equation the log $\dot{J}^e(t)$ curve should superpose precisely upon the log $\dot{J}^{eo}(t)$ curve with a horizontal shift of $-\log a_e$ and a vertical shift of $(\log a_e - \log b_e)$. There is now no rotation producing parameter of the b_e^{-1}
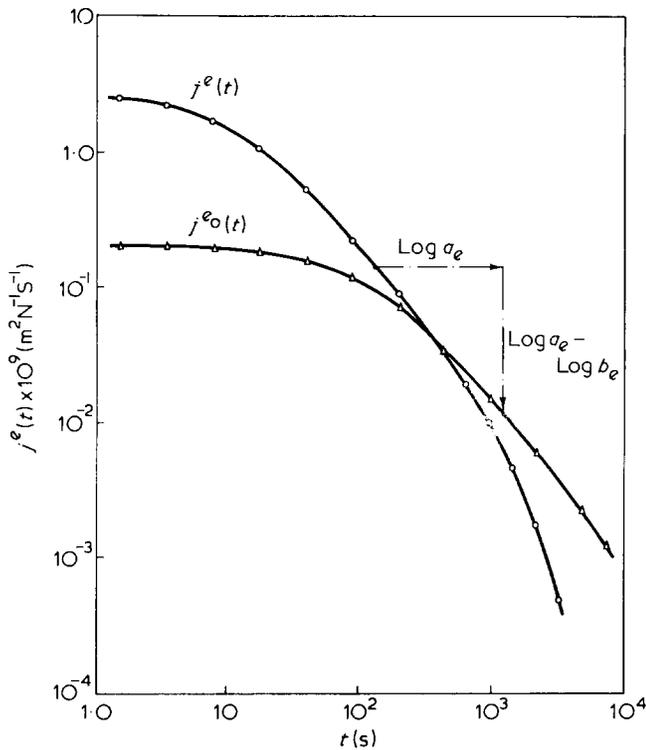
Figure 1 Illustration of the superposition procedure for $J^e(t)$: see equation 7. Data computed for the model described in the text with $a_e = 0.10$ and $b_e = 1.3$. The $J^e(t)$ curve superposes on the $J^{eo}(t)$ curve with a horizontal shift of $-\log a_e$ and a vertical shift of $(\log a_e - \log b_e)$

type in equation 6. To assist the reader we plot in *Figure 1* $\log J^e(t)$ curves computed from a simple purely illustrative and quite arbitrary model. The model comprises a set of nine Voigt elements distributed evenly, four per decade, and of equal strength. At reference elapsed time t_e^0 we take the relaxation strength for each element to be $\Delta J_0 = 1.0 \times 10^{-9}\text{m}^2\text{N}^{-1}$ with retardation times $\tau_0 = 10^N\text{s}$ with $N = 1.0$, 1.25, 1.50 ......, 2.50, 2.75 and 3.00. At an arbitrary elapsed time t_e we take the Voigt elements to be of strength $\Delta J = b_e\Delta J_0$ and of relaxation time $\tau^i = a_e\tau_0^i$. The rate of creep under stress σ at elapsed time t_e^0 is

$$\gamma^{eo}(t) = \sigma\Delta J_0 \sum_i \frac{\exp - (t/\tau_0^i)}{\tau_0^i}$$

so that

$$j^{eo}(t) = \Delta J_0 \sum_i \frac{\exp - (t/\tau_0^i)}{\tau_0^i}$$

At elapsed time t_e,

$$j^e(t) = b_e\Delta J_0 \sum_i \frac{\exp - (t/\tau^i)}{\tau^i}$$

In *Figure 1* a plot is shown of both functions with $b_e = 1.3$ and $a_e = 0.10$. The curves cross and the predictions of equation 7, of course, are observed. One curve superposes upon the other with the shifts indicated in *Figure 1*.

EXPERIMENTAL

Superposition experiment

The purpose of the experiment was to examine the concept of superposability using Methods 1–4 for $J^c(t)$ together with the more discriminating method based on $J^e(t)$, equation 7.

The specimen was a thin walled tube machined from a rod of isotactic polypropylene (Propathene PXC 8830) received from ICI Its density at 20°C was 0.905 g ml^{-1}. Before machining the rod was annealed at 130°C and slow cooled. It was mounted in a torsional creep machine[12] and surrounded by a cavity through which deionized water was passed at the required temperature. The specimen was heated at 80°C for 20 h, quenched to 40°C and maintained at that temperature. The quench was accomplished within seconds using fast T-jump equipment similar to that of Matthews and McCrum[16] but with the volume of the water-baths increased to 100 l to improve thermal stability. The first determination of compliance $J^e(t)$ was made for an elapsed time after the quench, t_e = 180s. The compliance was observed over a creep time 0–18s. The stress was then removed and the specimen allowed to recover. The recovery strain was observed in order to correct the strains in the second creep experiment which was initiated at t_e = 720s. Again the compliance was observed in the range of creep time t between 0 and $t_e/10$. This procedure was continued to a final elapsed time of t_e = 191 ks. This experiment follows closely that of Struik[1].

Thermally stimulated creep experiment (TSCr)

The TSCr experiment was designed to observe the effect of elapsed time at 15°C on long retardation times. Our procedure is based on that of Montpagens, Chatain and Lacabanne[17] (see also Turnhout[18] and Forgacs and Hedvig[19]). By an appropriate thermal and mechanical history the specimen is brought to 15°C with a packet of retardation times centred at $\tau \sim 3\text{Ms}$ 'tagged' by means of frozen-in strain. When the specimen is heated at a precisely controlled rate the frozen-in strain is released. If t_e at 15°C changes the retardation time then the temperature profile of the TSCr recovery curve will vary if t_e is varied.

The specimen of polypropylene which had been studied in the superposition experiments was heated at 80°C for one hour and then quenched to 60°C. After six min a stress of 0.828 MNm^{-2} was applied for 4000s. The stress was removed and precisely 40s later the specimen was quenched from 60 to 15°C, thus freezing in mechanical strain for a packet of elements with retardation times at 60°C centred in the region of 1 ks. The specimen was then mainatained at 15°C for t_e = 180s and then heated in a slow and controlled manner up to 80°C. As the specimen was heated the decay of the frozen-in strain was observed with a 7m throw of the optical lever. The experiment was repeated twice: in the second experiment, at 15°C the elapsed time was t_e = 720s and in in the third t_e = 7.2 ks.

In each experiment the controlled heating from 15°C was obtained by rotating the control knob of the water-bath thermostat with a clock-work motor at a precisely constant rate. The temperature was recorded every 2 min so that the remaining frozen-in strain was known at each temperature. The rate of change of temperature averaged between 15 and 80°C, dT/dt = 0.4° per min. The calibration of the thermostat knob was not quite linear but was highly reproducible. The rate of increase of temperature was therefore not linear but was exactly the same in each of the three experiments.
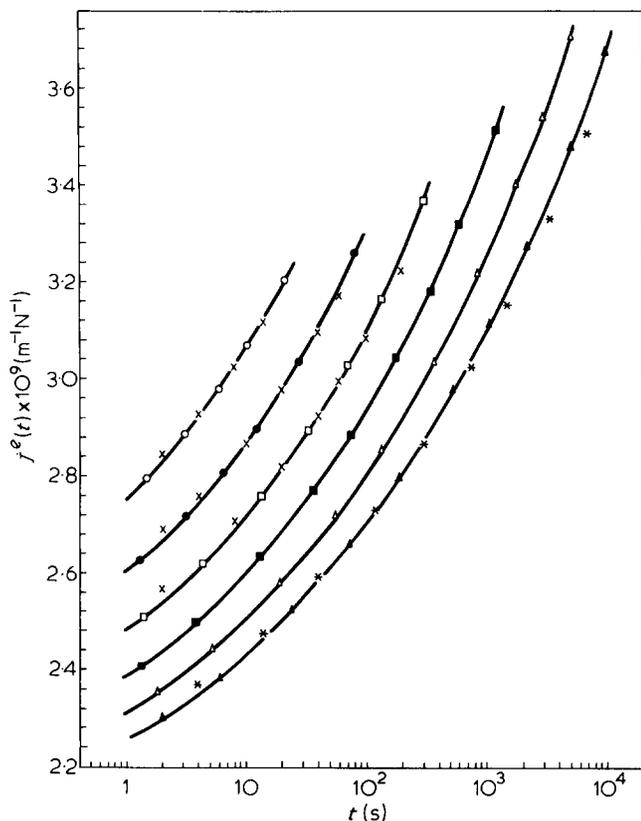
Figure 2 Dependence of the creep compliance $J^e(t)$ at 40°C on log t for six values of elapsed time t_e after quenching from 80°C: ○, 180s: ●, 720s: □, 2.9 ks: ■, 11.5 ks: △, 46 ks: ▲, 191 ks. The additional data marked by crosses are for the two subsidiary experiments described in the text to establish reversibility and the absence of mechanical enhancement. All shear strains below 3.06 × 10⁻³

Table 1 Values of shift factor a_e determined by Methods 1—4 and values of b_e obtained by Method 4 for various values of t_e

t_e(ks)	Method 1	Method 2	Method 3	Method 4	b_e
0.18	0.0125	0.036	0.0127	0.0629	1.147
0.72	0.037	0.070	0.039	0.100	1.090
2.9	0.100	0.124	0.100	0.167	1.043
11.5	0.240	0.243	0.234	0.309	1.023
46.1	0.530	0.540	0.521	0.623	1.017
191	1.0	1.0	1.0	1.0	1.0

The maximum strain at 60°C was 0.42 × 10⁻² and the strain frozen-in at 15°C, 0.11 × 10⁻². During its release in the heating to 80°C the pen of the graphispot recording the rotation of the optical lever covered just over 250 mm of chart paper. It was therefore quite simple to differentiate the curve by a difference procedure so that the rate of release of strain under the conditions of the experiment was known as a function of temperature.

RESULTS

Superposition experiment

The dependence of $J^e(t)$ on log t is shown in *Figure 2* for six values of t_e. It will be seen that the drop in compliance from t_e = 180s to t_e = 191 ks is ~20%. It was our intention in adopting 80°C as the temperature from which the specimen was quenched to eliminate as far as possible the likelihood of any small change in crystallinity. The annealing at 130°C before machining was also imposed partly to eliminate

possible change in crystallinity at lower temperatures. We take the effects exhibited in *Figure 2* to be physical aging as defined by Struik[1].

Reversibility[1] and the absence of mechanical enhancement[20−23] to aging was proved by two subsidiary experiments. In the first after quenching to 40 from 80°C, values of $J^e(t)$ were determined for values of t_e = 0.18, 0.72 and 2.9 ks. In the second after quenching to 40 from 80°C, values of $J^e(t)$ were determined only for t_e = 191 ks. It will be seen from *Figure 2* that the observations are highly reproducable and that the strains are sufficiently low (<3.06 × 10⁻³) for mechanical enhancement to be absent. The data in these two subsidiary experiments was not used further.

Shift factors were derived using superposition methods 1—4. The values of the shift factors so obtained are given in *Table 1* for reference elapsed time t_e^0 = 191 ks.

The superposed curves are shown in *Figures 3* and *4*. The master-curves obtained by the superposition procedures without vertical shift (Methods 1 and 3) were unsatisfactory. The master-curves obtained by Methods 2 and 4 appear smoother, as expected, since they were produced using the optimum fit criterion.

It will assist the reader if we state at once the difference between our attitude to the numbers recorded in *Table 1* and that of Struik[1]. In Struik's view, if the construction of the master-curve of optimum fit is mainly by horizontal translation this implies that the dominant effect is a shift in retardation time. The validity of this assumption is difficult to establish and rather uncertain. We shall therefore regard the numbers shown in *Table 1* as operational quantities whose philosophical implication is undetermined at present. This conservative attitude is based on the fact that the master-curves (even those produced by Methods 2 and 4) were all deficient in a systematic way, which we discuss after consideration of the differentiated curves.
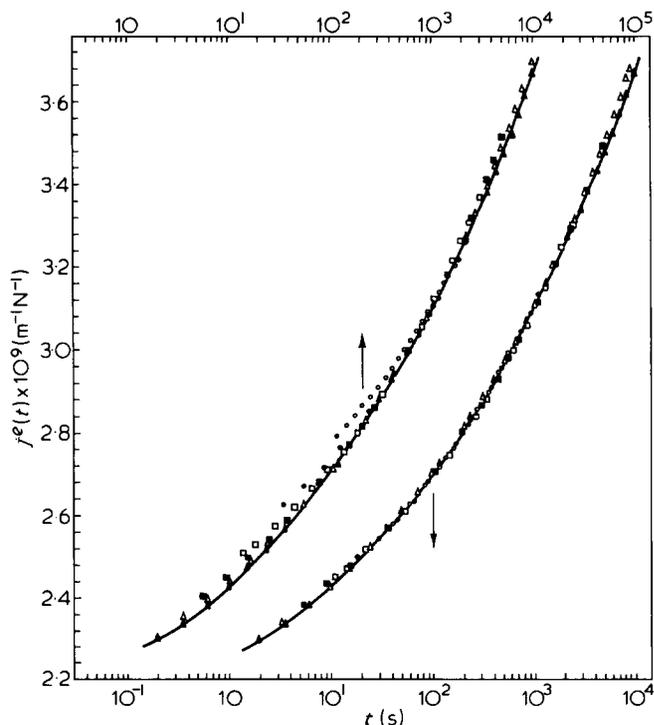
Figure 3 Data of *Figure 2* superposed by Method 1 (on the left) and Method 2 (on the right, displaced for clarity by one decade in time). Symbols as in *Figure 2*. Shift-factors given in *Table 1*
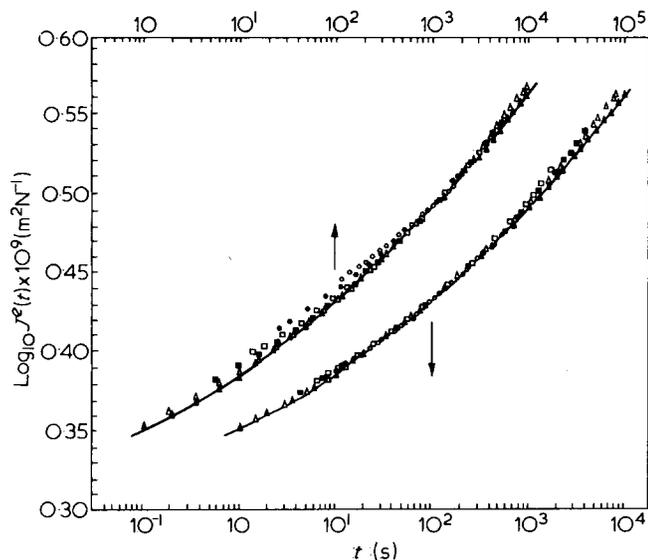
Figure 4 Data of *Figure 2* superposed by Method 3 (on the left) and Method 4 (on the right, displaced for clarity by one decade in time). Symbols as in *Figure 2*. Shift-factors given in *Table 1*
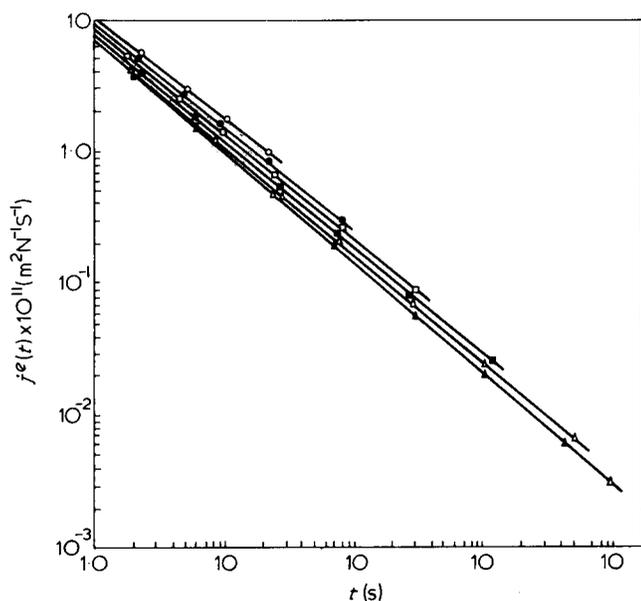
Figure 5 Dependence of log $J^e(t)$ on log t for the data of *Figure 2*. Symbols same as in *Figure 2*. The slopes of these straight lines are given in *Table 2*

The experimental data of *Figure 2* was differentiated by computer (Chen *et al.*[14] differentiation Method B) and is plotted against log t in *Figure 5*. On this log—log plot the data fit straight lines. The curvature of the illustrative model shown in *Figure 1* is not in evidence; the α-process in polypropylene is exceptionally wide, far wider than the two decades of the model. Values of the slopes q [$q = d(\log J)/d(\log t)$] are given in *Table 2*.

As t_e increases q changes systematically from -0.749 to -0.858. Since the log J versus log t plots are linear it follows from equation 7 (and of course the *a priori* assumptions on which it is based) that the lines must also be parallel, which they are not. This strikes at the basic premiss of superposition as shown in the Discussion.

Thermally stimulated creep experiment

The temperature dependence of the TSCr recovery rate is

shown in *Figure 6*. The peak in the frozen-in strain release rate occurs at 65°C independent of elapsed time at 15°C.

DISCUSSION

TSCr experiment

The course of the TSCr experiment may be displayed best with a model consisting of Voigt elements in series with a spring, as shown in *Figure 7*. Consider the ith retardation element of retardation time τ^i and strength ΔJ^i at 60°C. A stress σ applied for 4000s and then removed leads, 40s later, to a situation in which the ratio of strain in the ith element to the equilibrium strain under the same stress σ is

$$Z_i = \frac{\Delta J^i(t)}{\Delta J^i} = [\exp{-(40/\tau_i)} - \exp{-(4040/\tau_i)}] \qquad (8)$$

Table 2 Values of q the slope of the log J (t) versus log t plot (*Figure 5*) for various values of t_e

t_e (ks)	q
0.18	-0.749
0.72	-0.774
2.9	-0.788
11.5	-0.820
46.1	-0.842
191	-0.858
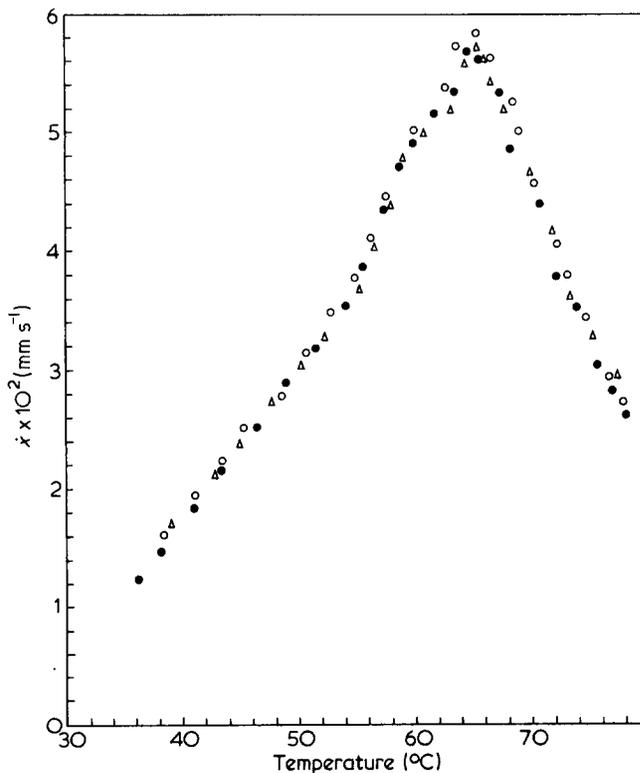
Figure 6 TSCr recovery curve for three values of t_e at 15°C: $\bigcirc$, 0.18 ks; $\triangle$, 0.72 ks; $\bullet$, 7.2 ks. $\dot{x}$ is the rate of change of the deflection of the optical lever. The conversion to rate of change of shear strain is $\dot{\gamma}$ = 4.807 x 10^{-6} $\dot{x}$. The maximum creep recovery occurs at 65° independent of t_e. Average rate of heating 0.4° per min
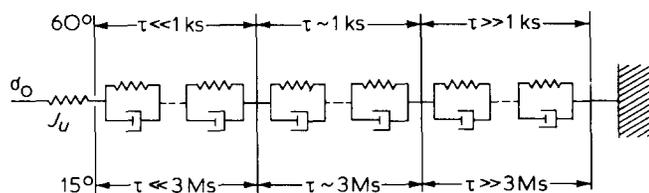
Figure 7 Interpretation of TSCr recovery experiment by series model. The frozen-in strain is produced by applying a stress at 60°C for 4 ks and switching it off for 40s: at this time a packet of elements are strained with $\tau \sim 1$ ks (*Figure 8*). The specimen is instantaneously quenched to 15°C at which temperature the same strained packet is centred at $\tau \sim 3$ Ms. The TSCr recovery experiment seeks to determine whether or not at 15°C increasing t_e causes the strained packet to move to retardation times in excess of 3 Ms
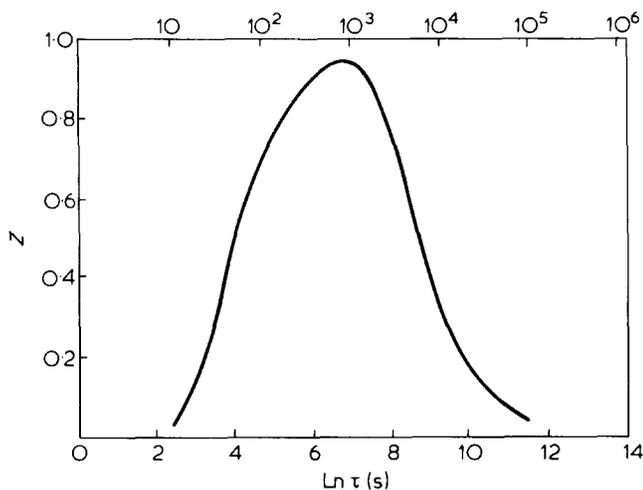
Figure 8 An estimate by viscoelastic model of the strain profile at 60°C (equation 8) at the instant before the quench to 15°C. The strained elements lie at $\tau \sim 1$ ks. After the quench to 15°C the strained elements lie at $\tau \sim 3$ Ms

The dependence of Z_i on $\ell n \tau$ is shown in *Figure 8*. The frozen-in strain profile at 60°C is centred in the region of 1 ks and is of half-width approximately two decades. Quenching the specimen from 60 to 15°C moves the centre of the strained packet to ca. 3 Ms (assuming a value $\Delta H = 35$ kcal mol^{-1} from single and double T-jump experiments[14] at 40°C). If increasing t_e at 15°C moves the spectrum as a whole to longer times, it will also move the tagged packet to longer times. In this case the peak in the TSCr recovery curve will occur at a temperature which will depend on t_e. But if, on the other hand, t_e does not move the spectrum as a whole, then the peak in the TSCr recovery curve will occur at a temperature which is independent of t_e at 15°C.

The essential argument is that exactly the same strain profile is frozen into the specimen at 15°C in all three TSCr experiments. That equation (8) may not yield exactly the precise frozen-in strain is not significant.

If the Struik hypothesis is correct the anticipated shift may be estimated as follows. An experiment was performed with an identical thermal pre-history to the TSCr experiment [80°C (1 h) ↓ 60°C (1.2 h) ↓ 15°C (t_e)]. At 15°C the shift factors a_e were measured: Method 1 gave $a_e = 0.0118$ for $t_e = 0.180$ ks and $t_e^0 = 11.5$ ks. If the $t_e = 0.180$ ks TSCr recovery curve peaks at 65°C then, if this measured a_e reflects a real shift in the retardation times, the $t_e^0 = 11.5$ ks peak should occur at ~ 94°C.

It will be seen from *Figure 6* that the values of t_e up to 7.2 ks at 15°C have no effect on the tagged packet: the

TSCr recovery curve peaks at 65°C independent of t_e. No conclusion can be drawn from this experiment on retardation times other than those in the tagged packet ($\tau \sim 3$Ms at 15°C). It would be of interest to know the effect of increasing t_e on the shorter retardation times effective in creep experiments.

The Struik hypothesis can explain the TSCr recovery data but with a somewhat forced argument. At 15°C the retardation times of the strained packet with increasing t_e move uniformly to longer times. When the specimen is heated up from 15°C there is a shift in the other direction, exactly cancelling the t_e induced shift at 15°C. Therefore the peak in the TSCr recovery curve occurs at 65°C independent of t_e. In our view the plausibility of this explanation is low.

We take the result of the TSCr experiment to be that physical aging does not change the retardation spectrum at long times and that a retardation element at τ is unaffected in magnitude or temporal position by elapsed time t_e for $t_e \ll \tau$. However, there are large changes in the spectrum at short times which are revealed in the superposition experiments.

Superposition experiment

As described in the Results section with respect to *Figure 5*, since the several $\log J^c(t)$ versus $\log t$ plots are straight lines with different slopes they cannot superpose according to equation 7. This is illustrated quantitatively in *Figure 9* for $t_e = 2.9$ ks and $t_e^0 = 191$ ks using values $a_e = 0.167$ and $b_e = 1.043$ obtained by Method 4 (*Table 1*). The points X and Y should transpose onto the reference line. However at X' the transposed line lies $\sim 10\%$ below the reference line and at Y' the transposed line lies $\sim 10\%$ above. This discrepancy in slopes is easily seen when performing the $J^c(t)$ superposition with large graphs in the laboratory and may be seen in the small scale graphs printed in *Figure 4*.
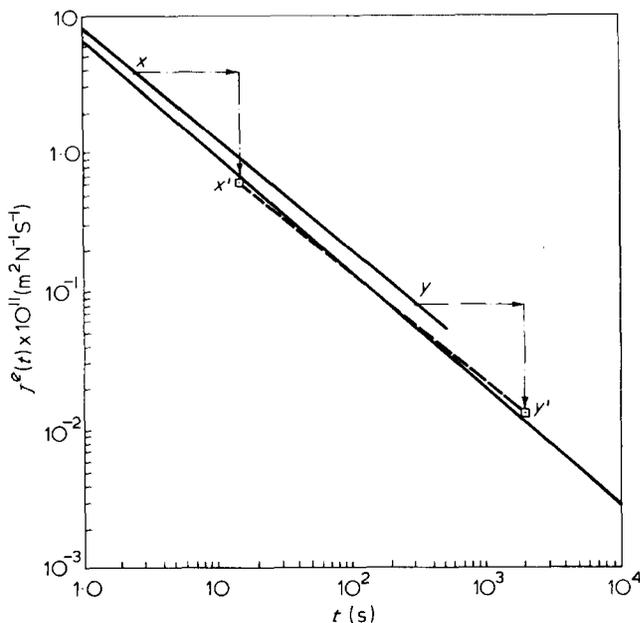
Figure 9 The two lines show the $\log J^e(t)$ versus $\log t$ data of *Figure 5* for $t_e = 2.9$ ks and $t_e^0 = 191$ ks. Th points X and Y on the $t_e = 2.9$ ks line should transpose onto the $t_e^0 = 191$ ks line with shifts calculated from equation 7 using the Method 4 values of $a_e = 0.167$ and $b_e = 1.043$ (*Table 1*). The indicated shifts move X to X' and Y to Y': X' lies 10% below the t_e^0 line and Y' 10% above. The systematic error in slopes can be seen also in the master-curve obtained by Method 4 (*Figure 4*).

For instance compare the t_e = 2.9 ks data with the t_e^0 = 191 ks data in *Figure 4*, Method 4. The vertical shift produces a matching of slopes in the centre of the run of data. but at the edges there is a marked discrepancy in slopes. The curves are not superposable.

It is clear therefore that equations (6) and (7) are not verified by experiment. This is due to the failure of the premisses upon which they are based. These are that a_e and b_e are constants applicable equally to all elements of the distribution function and defined for a specific thermal history and value of t_e. Following the quench it appears that the short time elements ($\tau \leqslant t_e$) of the retardation spectrum change either in magnitude or temporal position and possibly in both while the long time elements ($\tau \gg t_e$) do not change at all. Thus a_e and b_e depend on retardation time as well as elapsed time. The t_e induced change in shape of the retardation spectrum, observed just below T_g in amorphous polymers[5,6], occurs also in polypropylene in the α-region. It is certain that a similar effect must have occurred in the aging experiments of Hutchinson and Bucknall[24]

We have no evidence from these experiments whether the dominant aging effect is a change in relaxation magnitude or a change in retardation time. In linear polyethylene, aging experiments in the γ-region show the dominant effect to be change in relaxation magnitude. It is hoped that experiments in progress in our laboratory will throw light on this interesting and important problem.

Use of superposition for prediction at long times

In the light of Struik's experiments[1,2] and those reported here, prediction at long times by either $t-T^{25}$ or $t-t_e^1$ superposition can be made by empirial procedures which, although lacking a rigid theoretical foundation, may be of considerable utility. Because of the change in the shape of the retardation spectrum with t_e the superposition has no defined fundamental significance. But it is possible that at an operational level the procedures may be of use.

The effect of spectrum shape cahnge on the T-jump methods[14] for the determination of ΔH is under review. In these experiments the magnitude of the T-jump ($\sim \pm 3°$) is much lower than in aging experiments. In addition single T-jump ($T_0 \uparrow T$) and double T-jump experiments ($T_o \uparrow T \downarrow T_o$) would be perturbed in different ways if aging had an appreciable effect[14]. The experimental data suggest that the effect of spectrum shape change is very small, if not negligable. We will report on this important point elsewhere.

CONCLUSION

Physical aging proceeds by change in either the magnitude of the retardation function, in its temporal position or possibly in both. These changes depend on retardation time and occur the more quickly the shorter the retardation time. Therefore the shape of the retardation function changes with aging time so that superposition procedures are vitiated.

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