Mechanical relaxation in isotactic polypropylene

B. E. Read
Division of Materials Applications, National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK
(Received 21 November 1988; accepted 20 December 1988)

Empirical functions based on the Cole–Cole equation have been employed to model dynamic mechanical data obtained for isotactic polypropylene over a wide frequency range (10^{-2}–10^7 Hz) at temperatures between −10°C and 50°C. This analysis has yielded parameters characterizing the glass–rubber β-relaxation as a function of temperature. The relaxed compliance for the β-process increases appreciably with temperature in the range above 20°C. This result is attributed largely to changes in non-equilibrium structure, controlled by the α-relaxation, which erase the physical ageing effects produced during the initial storage at room temperature. Relaxation times for the β-process are essentially unaffected by these structural changes and vary with temperature according to the Vogel–Fulcher (or WLF) equation. The corresponding distribution of relaxation times narrows with increasing temperature. These results are largely consistent with Boyd's analysis of constant frequency, variable temperature, dynamic data for crystalline polymers. However, at temperatures $T \leqslant T_g (\sim -15°C)$ deviations from the Vogel–Fulcher equation are indicated by results obtained by McCrum using the thermal sampling technique. These deviations are ascribed to non-equilibrium amorphous-phase structures existing below T_g. Possible variations in these structures during thermal sampling experiments contribute to uncertainties about the significance of the proposed compensation rule for describing the temperature dependence of retardation times.

(Keywords: polypropylene; mechanical relaxation; dynamic moduli and compliances; physical ageing; Cole–Cole functions)

INTRODUCTION

In common with several other partially crystalline polymers isotactic polypropylene (PP) exhibits three relaxation regions labelled α, β and γ respectively[1–4]. These processes are observed in order ot decreasing temperature in plots of dynamic moduli and loss factors as a function of temperature at constant frequency. In the quantitative analysis of these isochronal plots it is difficult to separate the effects produced by changes in relaxation strengths, relaxation times and distributions of relaxation times, respectively, with temperature. However, assuming certain forms for the temperature dependence of the different relaxation parameters, Boyd has successfully modelled such data for a number of crystalline polymers on the basis of empirical Cole–Cole functions[4,5].

More recent investigations of isotactic PP have shown that changes in structure associated with physical ageing at temperatures $T > T_g$ (the glass transition temperature $\sim -15°C$) can substantially influence relaxation times for the α-process and relaxation strengths for the β-process[6–8]. Struik has also shown[6] that relaxation times for the β-process are strongly affected by physical ageing at temperatures below T_g.

As part of a study of relaxation processes and physical ageing in crystalline polymers, we have determined the components of the complex dynamic tensile modulus ($E^* = E' + iE''$) and compliance ($D^* = D' - iD''$) for isotactic PP over a wide frequency range (10^{-2}–10^7 Hz) at temperatures between -10°C and 50°C. The data relate principally to the glass–rubber β-relaxation involving the amorphous phase of the polymer. To obtain estimates of the relaxation parameters for the β-process as a function of temperature, isothermal plots of E', E'', D' and D'' *versus* log (frequency) have been analysed by means of Cole–Cole functions. The purpose of this paper is to present and discuss the results of this analysis in relation to the observed effects of physical ageing on the β-process and to the analysis of isochronal data for crystalline polymers. The observed dependence of retardation times on temperature will also be compared with the temperature-dependence of retardation times for $T \leqslant T_g$ derived by McCrum for the same PP material using the technique of thermally stimulated creep (or thermal sampling)[9].

EXPERIMENTAL

Material

The isotactic PP was supplied in the form of strips by Dr N. G. McCrum of Oxford University. These were machined from a rod of ICI Propathene PXC 8830 which had been prepared by very slow extrusion, annealed for an extended period at 130°C and cooled slowly to room temperature. The density of this material was 906.5 kg m^{-3} which corresponds[10] to a degree of crystallinity of about 65%. Prior to the dynamic measurements the strips were stored (aged) at room temperature for about 6 months.

Dynamic measurements

The methods used for determining the components of E^* and D^* comprised a tensile non-resonance (10^{-2}–10^2 Hz), a flexural resonance (160 Hz–4.4 kHz), a longitudinal resonance (5–10 kHz) and an ultrasonic

0032-3861/89/081439-07$03.00

pulse (1.1 and 2.8 MHz mean frequencies) technique. Full details of these methods, including corrections for errors, have been described previously[11,12]. Values of E' and D' obtained from the various methods are generally considered to be accurate to within 1–2% and values of $\tan\delta$ ($=E''/E' = D''/D'$) are usually known to within about 5%.

Preliminary observations revealed a reduction in E' values and increase in loss factors at room temperature after heating samples for periods (typically 1 h) necessary to complete the higher temperature measurements and cooling back to room temperature. The initial properties were gradually recovered after storing the sample at room temperature for a few months. Owing to this effect, which is ascribed to a deageing of the material on heating to above the storage temperature, measurements in the range 20–50°C were made (in order of increasing temperature) after completing the lower temperature (−10–+20°C) studies for each sample. At each temperature samples were maintained for about 30 min prior to making measurements.

ANALYSIS OF RESULTS

Figure 1 shows the dependence of E' and E'' on frequency f(Hz) at different temperatures between −10°C and 50°C. The corresponding D' and D'' data are presented in *Figure 2*. The broad dispersions in E' and D' and peaks in E'' and D'' observed for temperatures $T \geqslant 0$°C are attributed predominantly to the glass–rubber β-relaxation in PP which is usually found in the vicinity of 0°C from isochronal measurements around 1 Hz (refs. 1, 2). However, the onset of the higher frequency γ-process is apparent from the small rise in E'' at frequencies above 1 kHz at −10°C and could be partly responsible for the slight asymmetry of the E'' peaks at higher temperatures which tend to be broader on the high frequency side. The lower frequency α-process is also evident from the rise in D'' with decreasing frequency in the low frequency region for $T \geqslant 20$°C. This process is probably responsible for the slight asymmetry of the D'' peaks which are somewhat broader on the low frequency side. A short plateau on the D' curves at low to intermediate frequencies for $T \geqslant 20$°C marks the region between the β- and α-processes. The level of this plateau increases substantially with increasing temperature between 20°C and 50°C.

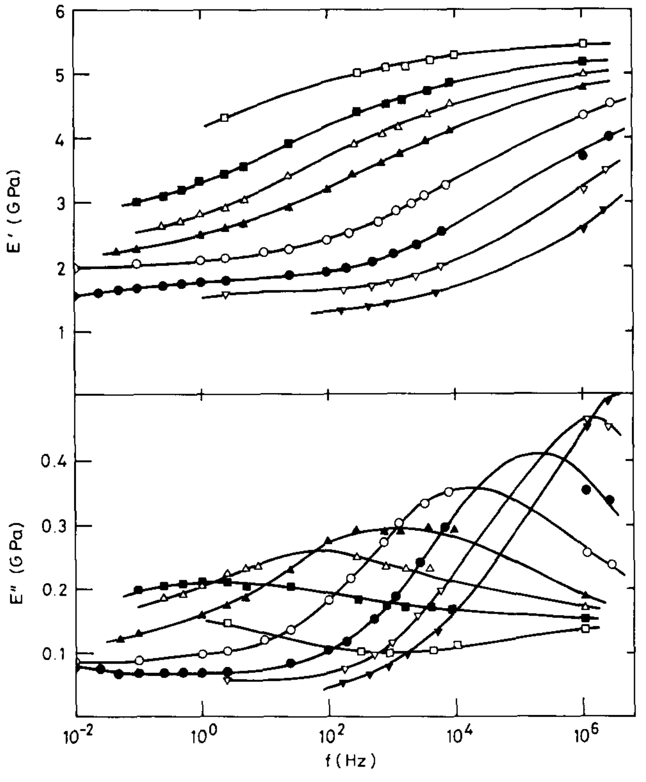

Figure 1 Variation of the tensile storage modulus E' and loss modulus E'' with frequency for isotactic polypropylene at different temperatures (°C): □, −10; ■, 0; △, 5; ▲, 10; ○, 20; ●, 30; ▽, 40; ▼, 50

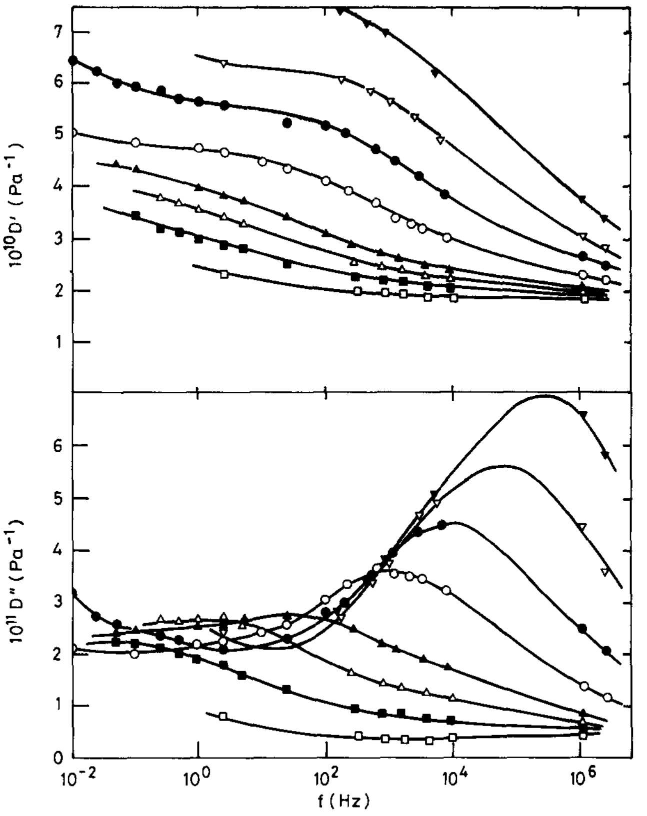

Figure 2 Frequency dependence of the tensile storage compliance D' and loss compliance D'' at different temperatures. Symbols are explained in *Figure 1*

Application of the Cole–Cole function

The results in *Figures 1* and *2* are conveniently analysed in terms of the empirical Cole–Cole equation which, by analogy with its use in dielectric studies[13], gives for the complex tensile compliance

$$D^* = D' - iD'' = D_U + \frac{(D_R - D_U)}{1 + (i\omega\tau_{CD})^n} \qquad (1)$$

where ω is the angular frequency ($2\pi f$) and $i = (-1)^{1/2}$. D_U and D_R are the respective unrelaxed and relaxed compliances, τ_{CD} a central (most probable) retardation time and n a parameter ($0 < n \leqslant 1$) characterizing the width of the retardation time distribution. Writing $E^* = 1/D^*$ for the complex tensile modulus it follows from equation (1) that

$$E^* = E' + iE'' = E_R + \frac{(E_U - E_R)(i\omega\tau_{CE})^n}{1 + (i\omega\tau_{CE})^n} \qquad (2)$$

where E_R ($=1/D_R$) and E_U ($=1/D_U$) are the relaxed and unrelaxed moduli and τ_{CE} a central relaxation time given by

$$\tau_{CE}^{n} = (D_U/D_R)\tau_{CD}^{n} \tag{3}$$

Separating the real and imaginary parts of equations (1) and (2) we obtain

$$D' = D_U + \frac{(D_R - D_U)[1 + (\omega\tau_{CD})^n \cos(n\pi/2)]}{1 + 2(\omega\tau_{CD})^n \cos(n\pi/2) + (\omega\tau_{CD})^{2n}} \tag{4}$$

$$D'' = \frac{(D_R - D_U)(\omega\tau_{CD})^n \sin(n\pi/2)}{1 + 2(\omega\tau_{CD})^n \cos(n\pi/2) + (\omega\tau_{CD})^{2n}} \tag{5}$$

$$E' = E_R + \frac{(E_U - E_R)(\omega\tau_{CE})^n[\cos(n\pi/2) + (\omega\tau_{CE})^n]}{1 + 2(\omega\tau_{CE})^n \cos(n\pi/2) + (\omega\tau_{CE})^{2n}} \tag{6}$$

$$E'' = \frac{(E_U - E_R)(\omega\tau_{CE})^n \sin(n\pi/2)}{1 + 2(\omega\tau_{CE})^n \cos(n\pi/2) + (\omega\tau_{CE})^{2n}} \tag{7}$$

Equations (4)–(7) predict that plots of D', D'', E' and E'' against log ω should have symmetrical shapes. From the differentiation of equation (5) we obtain

$$\tau_{CD} = (\omega_{D''_{max}})^{-1} \tag{8}$$

and

$$n = (4/\pi)\tan^{-1}\left(\frac{2D''_{max}}{D_R - D_U}\right) \tag{9}$$

where D''_{max} is the maximum value of D'' observed at angular frequency $\omega_{D''_{max}}$. From equations (4)–(7) it also follows that

$$D_U = D'_{max} - \left(D'^2_{max} - \frac{D''_{max}}{E''_{max}}\right)^{1/2} \tag{10a}$$

or

$$D_U = D'_{max} - \left(D'^2_{max} - \frac{D'_{max}}{E'_{max}}\right)^{1/2} \tag{10b}$$

and

$$D_R = 2D'_{max} - D_U \tag{11}$$

Here E''_{max} is the maximum value of E'' and D'_{max} and E'_{max} the values of D' and E' at the frequencies of maximum D'' and E'' respectively.

In fitting equations (4)–(7) to the experimental results at a given temperature, τ_{CD} was first calculated from the observed $\omega_{D''_{max}}$ using equation (8) and D_U and D_R were estimated on the basis of equations (10) and (11) from the measured D'_{max} and ratio D''_{max}/E''_{max} or D'_{max}/E'_{max}. E_U and E_R were then evaluated from D_U $(=1/E_U)$ and D_R $(=1/E_R)$. n and τ_{CE} were subsequently obtained using equations (9) and (3) respectively. The derived parameters, which will be presented in the following section, were then employed with the aid of computer programs to evaluate D', D'', E' and E'' as a function of frequency from equations (4)–(7).

As illustrated in *Figure 3*, the Cole–Cole functions provide a good overall fit to the data at 20°C apart from a region at low frequencies where overlap with the α-mechanism yields higher D'' and E'' values than those calculated for the β-process. At higher temperatures, increased effects of overlap from the α-relaxation are evident at low frequencies, as exemplified by the fits to the data at 40°C (*Figure 4*). At low temperatures, discrepancies between calculated curves and experimental data are observed on the high frequency side of the β-peak (see *Figure 5*) which may partly reflect the effects of overlap with the γ-relaxation. However, at all temperatures good fits are obtained over frequency ranges close to the frequencies of maximum loss. This follows from the fact that the measured compliance and modulus components at these frequencies were used in the calculation of relaxation parameters. Although the shape of the β-relaxation may differ somewhat from the symmetrical Cole–Cole form, it is considered that the

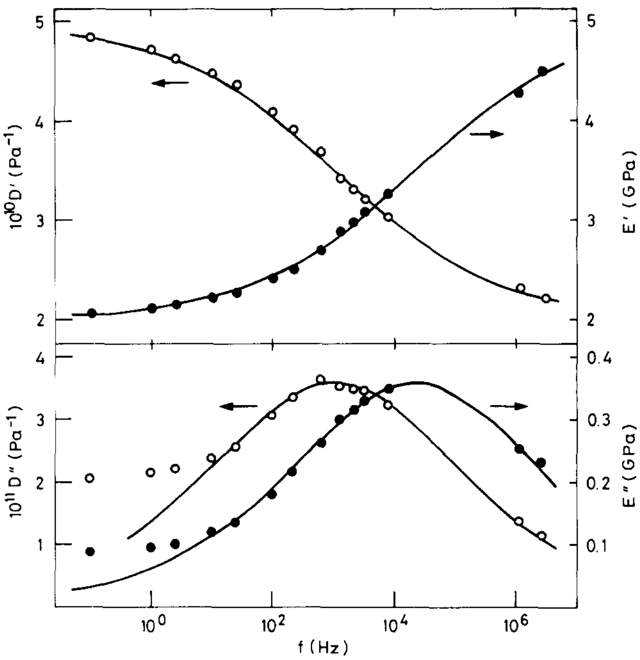

Figure 3 Comparison of experimental values of (○), D' and D'' and (●), E' and E'' at 20°C with theoretical curves (———) calculated from equations (4) to (7) respectively. $D_U = E_U^{-1} = 2.0 \times 10^{-10}$ Pa^{-1}, $D_R = E_R^{-1} = 5.0 \times 10^{-10}$ Pa^{-1}, $\tau_{CD} = 1.50 \times 10^{-4}$ s, $\tau_{CE} = 7.07 \times 10^{-6}$ s, $n = 0.30$

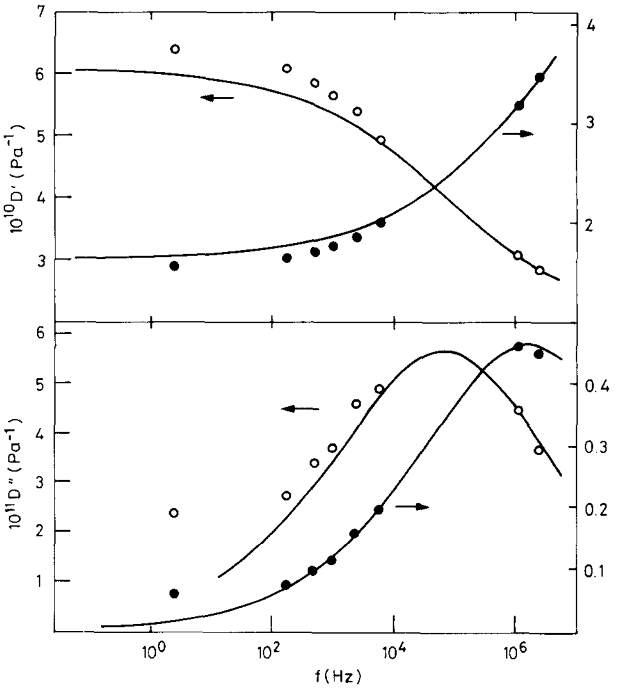

Figure 4 As for *Figure 3* except that the temperature is now 40°C and $D_R = E_R^{-1} = 6.1 \times 10^{-10}$ Pa^{-1}, $\tau_{CD} = 2.52 \times 10^{-6}$ s, $\tau_{CE} = 9.68 \times 10^{-8}$ s, $n = 0.34$

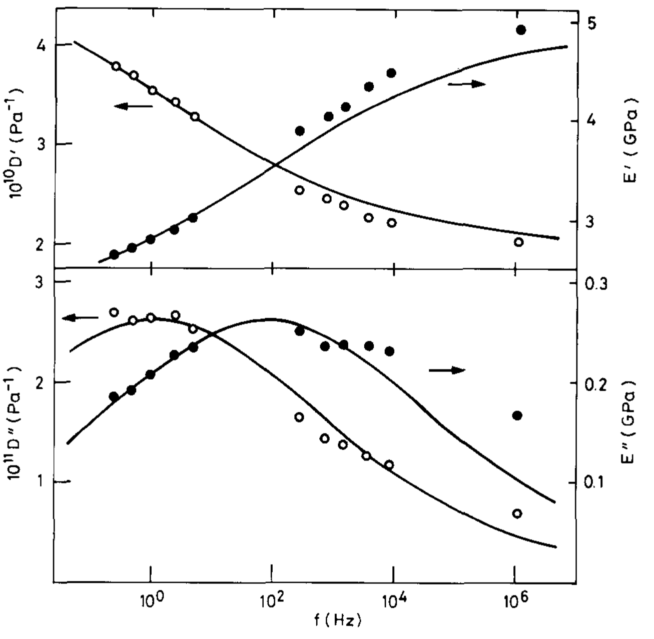

Figure 5 As for *Figure 3* except that the temperature is now 5°C and $\tau_{CD} = 1.26 \times 10^{-1}$ s, $\tau_{CE} = 1.96 \times 10^{-3}$ s, $n = 0.22$

derived parameters provide a fairly reliable characterization of the β-process and that the effects of overlap with the α- and γ-processes are minimized.

Magnitude and temperature dependence of relaxation parameters

In presenting the derived relaxation strengths for the β-process, we first note that the values of D_U (2.0×10^{-10} Pa^{-1}) and E_U (5.0 GPa) were constant within experimental error ($\pm 2\%$) over the temperature range investigated. This result is consistent with results of Boyd's analyses of isochronal data for highly crystalline polymers[5,14] which indicate that the temperature coefficient of log G_U for glass–rubber relaxations is of order -10^{-4}/°C.

At temperatures below 20°C the values of D_R and E_R were also essentially constant but in the range 20–50°C a marked increase in D_R or decrease in E_R was observed with increasing temperature. *Figure 6* illustrates these results and the corresponding temperature dependence of relaxation strengths $D_R - D_U$ and $E_U - E_R$. From the E_R results in this diagram we calculate d log E_R/dT $= -4.3 \times 10^{-3}$°C^{-1} at 30°C which compares well with the value d log G_R/d$T = -5.0 \times 10^{-3}$°C^{-1} at 27°C obtained by Boyd from an analysis of isochronal data for isotactic PP (ref. 4).

It will also be observed in *Figure 6* that the distribution parameter n increases from a value of 0.19 at 0°C to a value of 0.36 at 50°C. This result shows that the distribution is very broad in the low temperature region close to the glass transition but narrows appreciably with increasing temperature. However the value of n does not appear to depend linearly on temperature, as assumed by Boyd[5], but to increase more slowly as the temperature increases.

The temperature dependence of τ_{CD} and τ_{CE} has been analysed on the basis of the Vogel–Fulcher equation[15,16]

$$\log \tau = B + A/(T - T_\infty) \qquad (12)$$

where A, B and T_∞ are constants. This equation is equivalent to the Williams–Landel–Ferry (WLF) equation[17] and for $T > T_g$ provides a good description of the kinetics of the glass–rubber relaxation of amorphous polymers. Plots of log τ_{CD} and log τ_{CE} against $(T - T_\infty)^{-1}$ were constructed for different values of the adjustable parameter T_∞ and were found to be approximately linear for $T_\infty = 235 \pm 3$ K. The plots for $T_\infty = 235$ K (-38°C) are shown in *Figure 7* and yield

$$\log \tau_{CD} = -11.3 + 445/(T - 235) \qquad (13)$$

and

$$\log \tau_{CE} = -12.3 + 405/(T - 235) \qquad (14)$$

Within experimental error these results are consistent with a previous analysis[12] of tanδ curves from which we obtained $A = 1082/2.303 = 470$ and $T_\infty = 233$ K (-40°C) in an expression for $\tau_{\tan\delta}$ analogous to equations (13) and (14). Here $\tau_{\tan\delta}$ is the relaxation time obtained from the reciprocal angular frequency of maximum tanδ. The parameters in equation (13) are also consistent with the values $A = 446$ and $T_\infty = 233$ K (-40°C) obtained from creep data for amorphous atactic PP by Plazek and Plazek[18]. The non-Arrhenius temperature dependence of relaxation times expressed by equation (12) is also represented by the curved plot of log τ_{CD} against $1/T$ in *Figure 8*.

DISCUSSION

It should be recognized that the relaxation parameters for crystalline polymers may depend on thermal history because this has an important influence on the non-equilibrium structures at temperatures both above and below T_g (refs. 6, 7). From creep studies of isotactic PP I have found[8] that after rapid cooling from 80°C to

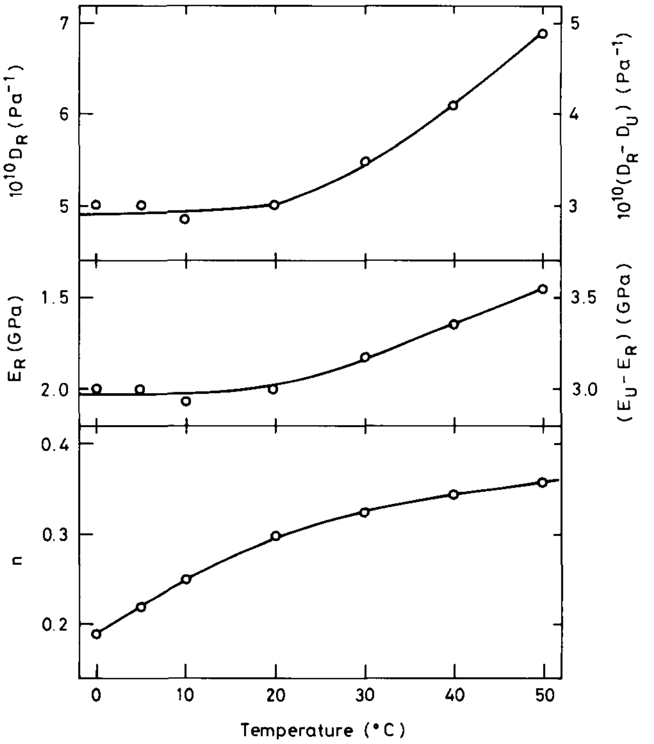

Figure 6 Temperature dependence of the relaxed compliance (D_R) and modulus (E_R), relaxation strengths ($D_R - D_U$) and ($E_U - E_R$) and distribution parameter n for the β-process. Results obtained from fitting the Cole–Cole functions to the dynamic data at different temperatures

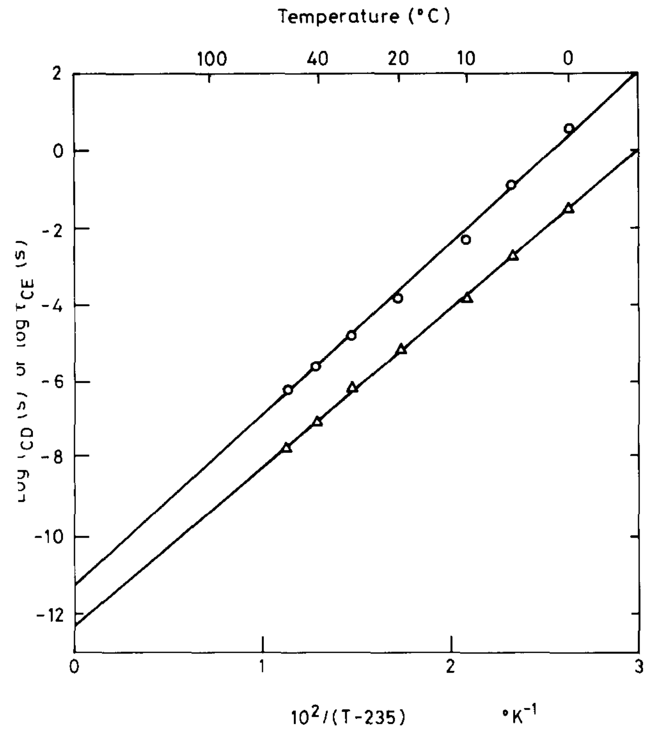

Figure 7 Temperature dependence of the most probable retardation time τ_{CD} (○) and relaxation time τ_{CE} (△) for the β-process, illustrating the validity of the Vogel–Fulcher equation (12)

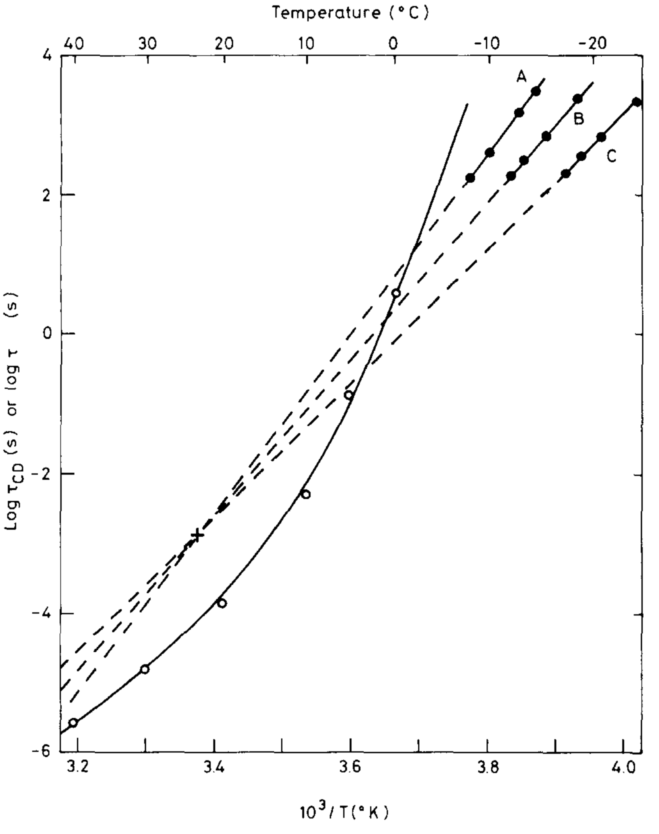

Figure 8 Temperature dependence of the most probable retardation time τ_{CD} (○) and the retardation times τ(●) obtained by McCrum from thermal sampling data. (A), $T_\sigma = -16.1$°C; (B), $T_\sigma = -21.9$°C; (C) $T_\sigma = -27.3$°C. Symbol + indicates the proposed compensation temperature $T_c = 23$°C

23°C ($T > T_g \approx -15$°C) the retardation times for the α-process slowly increase and the corresponding distribution broadens somewhat with increasing storage time at 23°C. These effects are accompanied by a substantial decrease in D_R and $D_R - D_U$ for the β-process but τ_{CD} and the distribution parameter n for the β-process are not significantly affected[8].

In discussing the possible origins of these physical ageing effects we consider temperatures T (e.g. 20°C) in the range $T_\alpha > T > T_g$ where T_α is the temperature of the α-relaxation (~ 100°C) determined in low frequency isochronal tests. Within this temperature region the molecular mobilities associated with the β- and α-processes are respectively very high and very low. Thus if the polymer is cooled to some temperature within this range the structure will rapidly attain equilibrium with respect to the β-process but not with respect to the α-process. Slow structural changes will then occur which are associated with the α-process and have been ascribed to molecular rearrangements in the amorphous phase which couple with the translation of polymer chains along the c crystal axes[8]. It was proposed that these conformational rearrangements yield more extended tie-molecules in the amorphous phase which serve to increase the activation energy and hence the retardation times of the α-process and simultaneously reduce D_R for the β-process[8]. If these slow conformational changes do not affect the motions of amorphous segments responsible for the glass–rubber β-process, then τ_{CD} for this process will be unaffected (as observed). It should be added that if a sample is reheated to temperatures above the storage temperature within the ageing range, the structural changes which occurred during storage are initially reversed and the sample is deaged prior to further ageing at the higher temperatures[7].

Before and during the dynamic studies of PP described in this paper, the annealed samples were maintained at temperatures between T_α and T_g. It follows that any influence of aged state on the β-process should be reflected only in the values of D_R or E_R and that n, τ_{CD} and τ_{CE} should be unaffected. Following the long period of storage at room temperature, it seems unlikely that significant further ageing would have occurred during the initial measurements between 0°C and 20°C. This suggestion is consistent with the observation (*Figure 6*) that D_R is essentially constant in this temperature interval, assuming that changes in D_R are negligible if the structure remains constant with respect to the α-process and at equilibrium with respect to the β-process. On subsequent heating to temperatures between 20°C and 50°C the marked increase in D_R with temperature may then be largely attributed to a deageing of the polymer, involving a reversal of the structural changes which occurred during the room temperature storage. This view is supported by the reduced values of E' and increased loss factors observed on cooling samples back to room temperature. Boyd's analysis of isochronal data for linear polyethylene[5] also yielded values of $-\mathrm{d}\log G_R/\mathrm{d}T$ for the β-process which increased sharply with temperature at temperatures just below 20°C and large values for this coefficient were obtained above room temperature for the β-relaxations of other crystalline polymers[4]. Because constant frequency measurements are usually effected in order of increasing temperature on samples initially stored at room temperature, these results may be related to the proposed deageing effects. The magnitudes and temperature coefficients of D_R and E_R will, of course, depend both on the previous thermal history and heating conditions during the dynamic measurements. These conditions are indicated in the experimental section for the data presented in *Figure 6*.

Although the increase of n with temperature (*Figure 6*) does not have the linear form assumed by Boyd[5], the applicability of the Vogel–Fulcher equation (12) to PP supports his use of this relation to characterize the temperature dependence of mechanical relaxation times for β-relaxations in crystalline polymers. This equation is valid, however, only for $T > T_g$ such that the polymer is in structural equilibrium with respect to the β-process. Attempts to determine a T_g value by differential scanning calorimetry were unsuccessful. This is attributed to the low magnitude and large width of the β-relaxation at low temperatures and may relate to highly perturbed amorphous chain conformations. On the basis of creep and dilatometric data for isotactic PP (ref. 19) deviations from equation (12) should be reflected by a gradual decrease in slope of the curved plot in *Figure 8* at temperatures below about -10°C. At these temperatures the local amorphous phase structure will no longer be at equilibrium with respect to the β-process for normal cooling rates. This arises from the marked decrease in mobility for the β-process and yields a dependence of β-retardation times on thermal history in this region.

Figure 8 includes some results obtained by McCrum[9] at temperatures $T \leqslant T_g$ using the thermal sampling technique on the PP material employed in our dynamic studies. With the thermal sampling method samples were subjected to a period of creep (at stress σ) and partial recovery at temperatures T_σ between -16.1°C and -27.3°C after slow cooling and ageing for 20 min at T_σ. The residual strains were then frozen into the material by quenching to $T_\sigma - 30$°C and measurements were subsequently made of the ratio strain/strain-rate as the strains recovered during heating at 2°C/min. For each T_σ an analysis of these measurements yielded the temperature dependence of the retardation time $\tau(T)$ characterizing the incremental part of the β-process stimulated by the stress history. *Figure 8* illustrates that $\log \tau(T)$ is a linear function of $1/T$ for the different retardation times within the distribution associated with the different T_σ. The slopes of these Arrhenius plots also increase with increasing $\tau(T)$ and upon extrapolation the plots all pass through the point with coordinates $\tau_c = 1.3$ ms and $T_c = 23$°C. Similar results have been obtained by this method for other amorphous and crystalline polymers and it has therefore been proposed that the kinetics of the glass–rubber relaxation follow a compensation rule given by[9,20]

$$\log \tau = \log \tau_c + \frac{\Delta H}{2.303R}[1/T - 1/T_c] \qquad (15)$$

where R is the gas constant and τ is some retardation time within the distribution having an activation enthalpy ΔH. According to this rule the distribution of τ arises from a distribution of ΔH so that the width of the distribution will vary with temperature. At the compensation temperature T_c all retardation times take the same value τ_c and the viscoelastic behaviour is characterized by a single retardation time.

From *Figure 8* it appears that the $\tau(T)$ values derived from the thermal sampling method correspond to the short-time side of the broad β-retardation spectrum for which the most probable retardation time is τ_{CD}. The apparent narrowing of the distribution of $\tau(T)$ with increasing temperature below 23°C also seems consistent with the increasing n values derived from the dynamic data (*Figure 6*). However the Arrhenius temperature dependence of $\tau(T)$ obtained from the thermal sampling technique contrasts with the non-Arrhenius behaviour observed from the dynamic results. Furthermore the suggestion that a single retardation time describes the viscoelastic behaviour at $T_c = 23$°C is inconsistent with the n values in *Figure 6*. These are much less than unity, illustrating that the β-retardation region is much broader than that for a single retardation time at all temperatures between 0°C and 50°C.

The above discrepancies almost certainly reflect the non-equilibrium structures which exist with respect to the β-process at temperatures below T_g and which influence the thermal sampling data. In this context we note that the entropy model of Adam and Gibbs predicts, with some approximation, an equation of the Vogel–Fulcher or WLF form at structural equilibrium ($T > T_g$)[21,22]. However for a constant structure at temperatures below T_g this theory predicts an Arrhenius temperature dependence of relaxation times with an activation energy which is larger when the structure is closer to equilibrium[23,24]. The higher ΔH values indicated by the thermal sampling data for the longer retardation times in the distribution might reflect a structural change toward equilibrium with increasing T_σ. Alternatively it is possible that the distribution of ΔH could refer to a constant structure produced by the constant ageing times at the different T_σ. In this case the compensation rule might serve to characterize the pure contribution of temperature to the retardation time changes at constant structure. However this suggestion is of doubtful validity owing to the uncertain structures and possible structural changes during heating in the glass transition region, the narrow temperature range covered by the thermal sampling data and long extrapolations involved.

CONCLUSIONS

Parameters characterizing the mechanical β-relaxation in isotactic polypropylene can be reliably estimated by fitting Cole–Cole functions to dynamic data over a wide frequency range.

The strength of the β-relaxation depends on non-equilibrium structures affected by the thermal history of the polymer at temperatures above T_g. Relaxation times for the β-process are influenced by thermal history only in the range $T \leqslant T_g$.

ACKNOWLEDGEMENTS

The author thanks Dr N. G. McCrum for supplying the polypropylene samples, Mr N. G. Savill for assistance with the low frequency, non-resonance measurements and Mr S. C. Read for the programming of functions employed in the data analysis.

REFERENCES

1 Flocke, H. A. *Kolloid Z.* 1962, **180**, 118
2 Passaglia, E. and Martin, G. M. *J. Res. Natl. Bur. Stand.* 1964, **68**, 519

3 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London (1967)
4 Boyd, R. H. *Polymer* 1985, **26**, 323
5 Boyd, R. H. *Macromol.* 1984, **17**, 903
6 Struik, L. C. E. *Polymer* 1987, **28**, 1521
7 Struik, L. C. E. *Polymer* 1987, **28**, 1534
8 Read, B. E., Dean, G. D. and Tomlins, P. E. *Polymer* 1988, **29**, 2159
9 McCrum, N. G. *Polymer* 1984, **25**, 299
10 Miller, R. L. in 'Encyclopedia of Polymer Science and Technology', Vol. 4 (Ed. N. Bikales), Wiley, New York (1966)
11 Read, B. E. and Dean, G. D. 'The Determination of Dynamic Properties of Polymers and Composites', Adam Hilger, Bristol (1978)
12 Read, B. E., Dean, G. D. and Duncan, J. C. in 'Physical Methods of Chemistry' (Eds. B. W. Rossiter, J. F. Hamilton and R. C. Baetzold), Wiley-Interscience, New York, Vol. VII, ch. 1, in press
13 Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1941, **9**, 341
14 Boyd, R. H. and Aylwin, P. A. *Polymer* 1984, **25**, 340
15 Vogel, H. *Physik. Z.* 1921, **22**, 645
16 Fulcher, G. S. *J. Am. Ceram. Soc.* 1925, **8**, 339
17 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
18 Plazek, D. L. and Plazek, D. J. *Macromol.* 1983, **16**, 1469
19 Hideshima, T. *Rep. Prog. Polym. Phys. Jpn.* 1962, **5**, 103
20 Lacabanne, C., Chatain, D., Monpagens, J. C., Hiltner, A. and Baer, E. *Solid State Commun.* 1978, **27**, 1055
21 Adam, G. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139
22 Ward, I. M. 'Mechanical Properties of Solid Polymers', Wiley, Chichester (1983)
23 Kovacs, A. J., Hutchinson, J. M. and Aklonis, J. J. in 'The Structure of Non-Crystalline Materials' (Ed. P. H. Gaskell), Taylor and Francis (1977), p. 153
24 Scherer, G. W. *J. Am. Ceramic Soc.* 1984, **67**, 504