Stress relaxation and time/temperature superposition of polypropylene fibres

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The viscoelastic properties of polypropylene fibres are investigated in a single-step stress relaxation test for small strains at temperatures between -50 and $+30°C$, thus well encompassing the glass transition temperature. For the analysis of the curves a formal two-component (TC) model is applied, which comprises an elastic and a viscoelastic component, the time-dependence of which is described by a relaxation function on the basis of a cumulative log-normal distribution; the shape of this was found to be independent of temperature. The component moduli, as well as the characteristic relaxation time, show pronounced temperature-dependencies. Above the transition temperature, at ca. $-15°C$, they all follow Arrhenius relationships, with activation energies which lie between -10 and $-30 \, kJ \, mol^{-1}$. The consistency of the analytical model is checked against the results of dynamic extensional tests, which furthermore enable us to identify the process as the α-transition in isotactic polypropylene. Evaluation of the properties of the components of the TC model in relation to the polymer morphology suggests that the relaxation process resides in the restricted amorphous phase of the material.

INTRODUCTION

For assessment of the applicability of certain polymers as engineering materials the time/temperature superposition principle, namely the superposition of relaxation or creep curves on the log-time scale, is of central importance, since it is the basis, together with the principles of physical ageing[1], for the prediction of long-term viscoelastic performance from comparatively short-term tests at various temperatures. Since the superposition apparently works well for a variety of polymers, whether they are elastomeric, thermoplastic, partially crystalline, or even filled[2,3], it is considered not to be just an arbitrary data reduction method. However, there are cases where authors raise doubts as to whether the technique is in reality suitable for predicting the long-term behaviour of polymeric constructional materials, and obvious difficulties with the approach are observed in the case of semicrystalline polymers, as reviewed by Schapery[4] and Boyd[5].

From an experimental point of view, this paper is concerned with the temperature dependence of the viscoelastic properties of polypropylene fibres for strains within the range of linear viscoelasticity. The investigation comprised the measurement of the behaviour of fibres in a single-step stress relaxation test over a sizeable temperature range (-50 to $30°C$) around the glass transition temperature, which is expected to occur at around $-10°C$, and for times of up to 8×10^3 s. The similarities with the experiments conducted by Faucher[6] are worth noting.

The main emphasis, however, is placed on the theoretical aspect, namely the question as to what extent a two-component (TC) model, as implied in the standard theory of linear viscoelasticity[7], may be validly applied in the relaxation modulus analysis. This approach is based on previous investigations related to the influence of the strain level on the stress relaxation performance of various types of fibres, including polypropylene[8,9], where this model was successfully applied.

The TC model comprises an elastic and a time-dependent, viscoelastic component. A special feature of the model is the use of the cumulative log-normal distribution (CLND) function as a relaxation function with a shape which is not only found to be independent of temperature but is also consistent with the universal shape[8] found, for a wide variety of materials, by Kubat[10].

The application of the model reveals the temperature dependence of the component moduli and of the mean relaxation time for the α-relaxation process in isotactic polypropylene, all of which may be described by Arrhenius relationships. The shift of the relaxation function with temperature is consistent with a simple non-cooperative relaxation process, which is activated at a transition temperature of approximately $-15°C$.

EXPERIMENTAL ASPECTS AND DATA BASIS

The single-step stress relaxation test is one of the simplest methods for the examination of viscoelastic materials[7]. In the present case, a single fibre is deformed within a short period of time, $\Delta t \leqslant 5$ s, to a predetermined strain, $\varepsilon < 2\%$, at a constant rate of deformation (e.g.

20% min^{-1}. The strain is given by the following:

$$\varepsilon = \Delta l/l_0 \qquad (1)$$

where Δl is the change in length and l_0 is the initial specimen length. These two parameters were determined according to the principles outlined in ASTM D2101[11] and as described in detail in ref. 8.

Subsequently, the strain is held constant and the drop in the resulting force F is followed with time, where the start of the experimental time-scale, $t = 0$, is taken as the end-point of the straining step where $F = F(0)$.

The relaxation modulus, $E(t)$, for a given cross-section of fibre, A, is given by the following:

$$E(t) = F(t)/(A\varepsilon) \qquad (2)$$

In this context, $E(0) = F(0)/(A\varepsilon)$ will be referred to as the experimental modulus of the fibres.

The polypropylene fibres that were investigated are a commercial product used for textile purposes (Vestolen P2000 CR, Chem. Werke Hüls AG). The material is largely isotactic (95%) and partially crystalline ($\sim 50\%$).

The thermomechanical transitions of the material are well defined in a dynamic torsion experiment according to DIN 53445[12], kindly conducted by the manufacturer (Chem. Werke Hüls AG), as a logarithmic decrement (log Λ) peak between ca. -10 and $+30°C$ with its maximum at $+8°C$, and a further, less well defined, broader peak at $\sim 90°C$, which, following Boyd's[5] terminology, are identified as the β- and α-relaxation, respectively.

Prior to the stress relaxation experiment the cross-sectional area of each fibre was determined at room temperature using a vibroscope (Fa.Insco). The mean diameter was determined (on the basis of 200 fibres) as 20.7 μm, with a standard deviation of $s = 1.64 \mu$m. No correction was applied to account for the change of the cross-sectional area with temperature.

All experiments were conducted on an Instron (Type 1122) tensile testing machine under standard climatic conditions (22°C, 65% r.h.). To increase the force signal and to facilitate fibre alignment, the fibres were examined in the form of loops (50 mm overall length) that were led over a stainless steel hook (1.5 mm diameter) connected to the load cell. The ends of the loop were secured by an appropriate clamping arrangement to the moving cross-head of the machine. The clamping arrangement was enclosed in a glass cylinder for which a temperature-controlled jacket ensured a constancy of the temperature within less than $\pm 1°C$. Appreciating the limitations of the experimental set-up for the material being investigated, the temperature range was chosen as -50 to $+30°C$, which well encompassed the expected glass transition of the material. After clamping the fibre, the set-up was inserted into the cylinder and then kept at the temperature of measurement for 2 h for equilibration purposes prior to experimental measurements being made.

To minimize influences due both to relaxation during the straining step and also to experimental background effects, which become significant with longer experimental times, only data in the range $\Delta t < t < 8 \times 10^3$ s were used for the analysis. The upper limit of strain was set at 2%, as a generous, but nevertheless reasonable interpretation of the linear viscoelastic performance of the fibres[8].
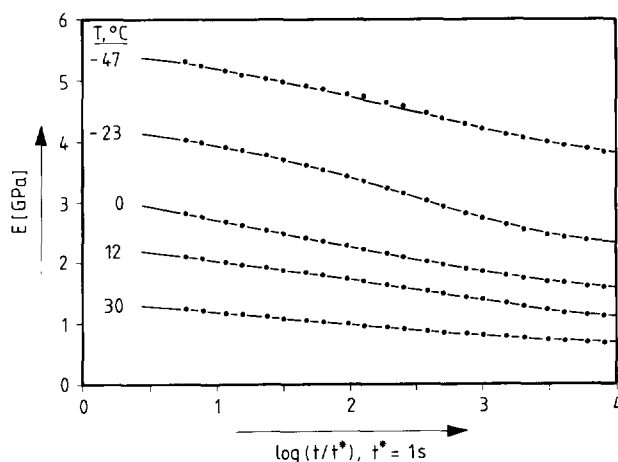

Figure 1 Typical relaxation modulus/log(time) curves obtained for the investigated temperature range; the solid lines relate to the theoretical description of the relaxation curves, based on $z = 4.5$ (see equation (4))

Figure 1 summarizes a representative set of curves presented as modulus vs. log(time) plots. The solid lines through the data points represent the theoretical description, which will be presented below.

The extensional, dynamic mechanical test (see later) was conducted on a Gabo Qualimeter (Fa. Gabo) at 2 Hz and at a static strain of 1% with a superimposed dynamic strain of $\pm 0.4\%$, over the temperature range of $\pm 100°C$.

ANALYSIS MODEL AND RESTRICTIONS

A description for the linear viscoelastic behaviour of polymers in stress relaxation, consistent with the approach described in ref. 7, is given by the following:

$$E(t) = E_\infty + \Delta E \Psi(t) \qquad (3)$$

This approach comprises two components, an elastic component E_∞ and a transient component with a limiting elastic modulus ΔE, the time dependence of which is given by the relaxation function, which is described here by using the cumulative log-normal distribution (CLND) function[8], given for the natural log(time) scale by the following:

$$\Psi(\ln t) = 1/(\sqrt{2\pi}z) \int_{\ln t}^{+\infty} \exp\{-0.5[(x - \ln \tau_c)/z]^2\}dx \qquad (4)$$

where τ_c is the characteristic relaxation time, $\ln \tau_c$ is the mean, and z is the standard deviation of the underlying log-normal distribution; x is the integration variable on the ln(time) scale. The function $\Psi(\ln t)$ forms a strictly symmetrical, S-shaped curve which drops from unity to zero within a range of ca. $\ln \tau_c \pm 4z$. The initial modulus, E_0, relating to the situation where $\Psi = 1$, is given according to equation (3) by $E_0 = E_\infty + \Delta E$.

Applying the principles of the usual graphical procedure[13] a computer program was used to fit the CLND function to the data for $\Psi(\ln t)$ by a weighted linear regression procedure for optimized values of E_∞ and ΔE. Details of this procedure are given in ref. 8.

The model described by equations (3) and (4) will be referred to as the two-component (TC) model. Apart from

the choice of the relaxation function the model is formally consistent with the approach of Read[14] for the analysis of the β-relaxation of isotactic polypropylene on the basis of its dynamic mechanical properties.

Semicrystalline polymers may, on a simplified level, be considered as two-phase systems, comprising a fraction of polymer crystals embedded in an amorphous matrix (e.g. ref. 15). Linking this morphological two-phase approach and the TC model, E_{∞} may be considered as being the mechanical response of the crystalline fraction, which is determined by its material properties, its structure, the amount, and the overall orientation. The time-dependence of the limiting elastic modulus of the amorphous phase, ΔE, is described by $\Psi(t)$. A possible, elastic, lower-limiting modulus of the amorphous phase is neglected in these considerations. The change of the modulus of the crystalline phase in semicrystalline polymers with temperature was investigated in detail by X-ray measurements for various polymers in an extended series of papers by Nakamae and coworkers. For isotactic polypropylene[16] they found that the elastic modulus parallel to the chain axis of the crystalline phase was constant, at 33.3 GPa, up to $\sim 100°C$, while the modulus perpendicular to the chain axis showed a pronounced temperature-dependent decrease.

Generalizing these observations it appears necessary to assume that both of the elastic moduli in the TC model are temperature-dependent, with both expected to decrease with increasing temperature. This approach is analogous to that of McCrum and Morris[17], who allow for independent changes of the initial and limiting compliance when analysing the creep performance of poly(methyl methacrylate), and furthermore, are consistent with the observation by McCrum[18] that the intensities of the creep processes in polypropylene are temperature-dependent.

By fitting the TC model to the individual relaxation curves, the values for E_{∞}, ΔE, $\ln \tau_c$, and z were determined. *Figure 2* summarizes the values obtained for z as the parameter describing the shape of the relaxation function on the ln(time) scale over the range -50 to $+30°C$.

The results of this unrestricted fit show a considerable scatter, giving a mean of $s=4.4\pm0.22$ (95% confidence limits). Although the standard deviation does not exhibit

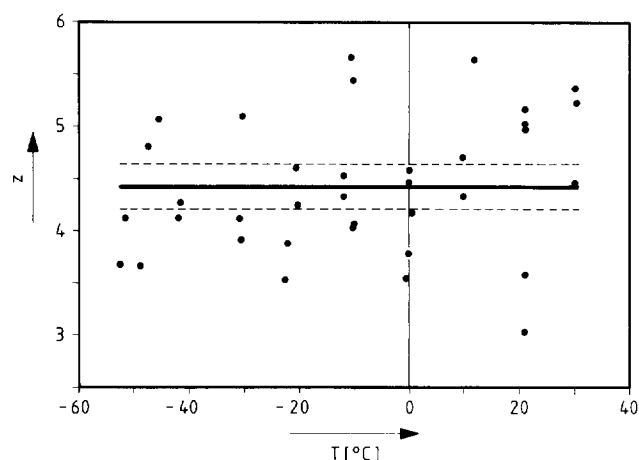**Figure 2** Values for the standard deviation, z, of the CLND function on the ln(time) scale, obtained from fitting the TC model to the experimental relaxation curves at various temperatures; the solid line represents the mean, and the broken lines the 95% confidence limits

a similarly pronounced instability, as observed for the strain-induced non-linear viscoelastic performance of polypropylene fibres[8], its variability nevertheless provides a major contribution to the scatter in the values of the other parameters. To suppress this part of the scatter the shape of the relaxation function is restricted to a constant, temperature-independent value of z, which, due to the lack of significance of the last digit, is chosen for the ln(time) scale as $z=4.5=1.95\ln(10)$, which is in good agreement with previous findings for Kevlar[R], Nomex[R], Technora[R], and polypropylene[8,9]. Furthermore, $z=4.5$ describes a shape for the relaxation function[8] that closely approaches that found by Kubat (e.g. ref. 10) for a large variety of different materials, including metals and polymers. The restriction to $z=4.5$ was thus introduced for fitting equations (3) and (4) to the experimental data.

Introducing a constant value for z implies, furthermore, that for the relaxation function the temperature effects are subject to the restriction that a change in temperature affects all relaxation times in a way, which is described by a temperature-dependent, multiplicative factor. This is also the assumption inherent in the theory of thermorheologically simple (TRS) and complex (TRC) materials (e.g. ref. 4). It is, furthermore, in accordance with the experimental observations made by Fytas and Ngai[19] and by Plazek and Plazek[20] for amorphous polypropylene. However, the constancy of z is in contrast to the implications of the compensation rule found, by McCrum[18], to be applicable for the α- and β-relaxation in isotactic polypropylene.

The restriction of the shape of the relaxation function and the assumed temperature-dependence of the component moduli lead to a generalization of equation (3) as follows:

$$E(t,T) = E_{\infty}(T) + \Delta E(T)\Psi(t,T) \tag{5}$$

which may be normalized to give the following:

$$E(t,T) = h_{\infty}(T)E_{\infty}^{R} + h_{\Delta}(T)\Delta E^{R}\Psi(t/a_T) \tag{6}$$

where E_{∞}^{R} and ΔE^{R} are the component moduli at a reference temperature. Their temperature functions $h_{\infty}(T)$ and $h_{\Delta}(T)$ are defined as follows:

$$h_{\infty}(T) = E_{\infty}(T)/E_{\infty}^{R} \tag{7}$$

and

$$h_{\Delta}(T) = \Delta E(T)/\Delta E^{R} \tag{8}$$

The acceleration factor, $a_T(T)$, is given by the following:

$$a_T = \tau_c(T)/\tau_c^{R} \tag{9}$$

where τ_c^{R} is the characteristic relaxation time at the reference temperature.

It follows from equation (6) that the properties of the viscoelastic component can be isolated by subtraction of the elastic component from the overall modulus, as follows:

$$E(t,T) - h_{\infty}(T)E_{\infty}^{R} = h_{\Delta}(T)\Delta E^{R}\Psi(t/a_T) \tag{10}$$

Equation (10) describes the relaxation curves obtained

for a so-called thermorheologically complex (TRC) material that on a log/log scale can superimpose as the result of rigid horizontal and vertical shifts. Boyd[5] emphasizes the necessity of this approach for highly crystalline polymers and Schapery[4], furthermore, suggests that the horizontal shift primarily reflects the temperature-dependence of the amorphous region, while the vertical shift accounts for changes in the rigidity of the crystalline regions. A model is thus proposed that for the viscoelastic component alone predicts TRC behaviour.

RESULTS

The experimental data displayed in *Figure 1* reveal that a well defined, isolated relaxation process was being investigated. *Figure 3* summarizes the results obtained for the experimental fibre modulus, $E(0)$ vs. temperature. The data show a continuous decrease with only a slight, if any, indication of a discontinuity of slope in the glass transition range. The initial modulus, E_0, is in all cases only slightly higher than the experimental value $E(0)$, so that irrespective of temperature, only a little amount of relaxation takes place during the straining step.

Analysis of the experimental curves enables the determination of the moduli of the components of the TC model and of the characteristic relaxation times, E_∞, ΔE, and τ_c, which are plotted as a function of temperature in *Figures 4* and *5*. The solid lines drawn through the data are introduced to illustrate the gradual change of the moduli with temperature.

Figure 4 shows a continuous decrease in E_∞ from 3–4 GPa down to ~ 0.5 GPa over the temperature range that was investigated. The ΔE data show a comparable, though slightly less overall change between ~ 3 and 1 GPa. The data obtained for log τ_c (*Figure 5*) follow a straight (or slightly curved) line, corresponding to characteristic relaxation times between ~ 1000 and 30 s, with no obvious indication of a transition being shown in this plot.

As implied in equation (10) the contributions of the viscous component can be superimposed in a log ΔE *versus* log t plot by vertical and horizontal shifts relating to log h_A and log a_T, respectively, thus enabling a visual control of the quality of the analysis procedure. The relaxation mastercurve for the curves displayed in *Figure 1*, for a reference temperature of $-47°C$, is shown
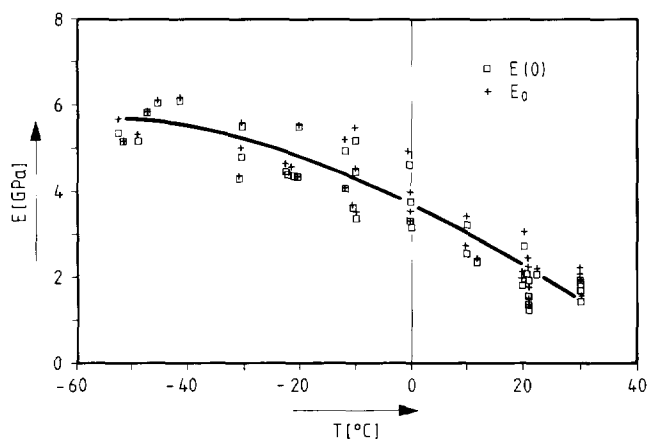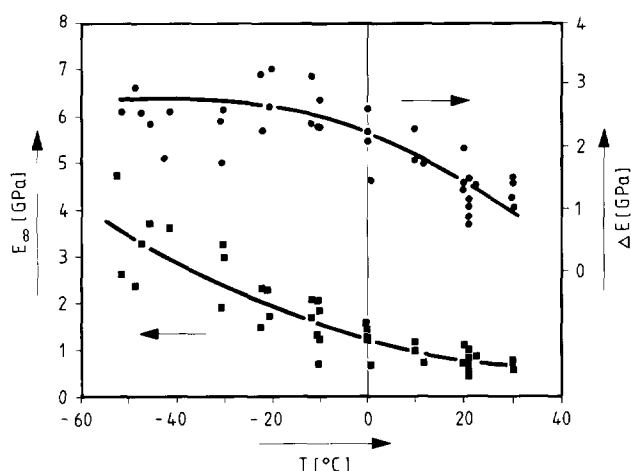

Figure 4 Elastic moduli of the elastic and viscous phases of the TC model. E_∞ and ΔE, respectively, *versus* temperature
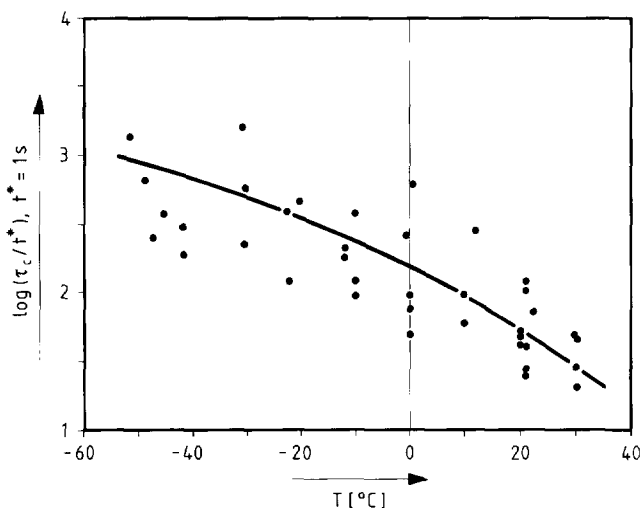

Figure 5 Characteristic relaxation time (plotted as log τ_c) *versus* temperature

in *Figure 6*. It covers four decades of time and about one order of magnitude for the modulus of the viscous component. The quality of the superposition of the data from the five experimental curves documents the quality of the analysis procedure. The quality of the mastercurve is considerably better than we can achieve for our curves by simple horizontal superposition of the E *versus* log t curves[21], and is certainly comparable in quality to the superposition achieved by Faucher[6] in a log(modulus) *versus* log(time) plot, applying the TRS principle to his data.

To assess the nature of the temperature-dependence of the variables of the TC model, Arrhenius plots for E_∞ and ΔE, are presented in *Figure 7*, with τ_c shown in *Figure 8*.

The data for E_∞ follow a straight line over the whole temperature range, where the slope is equivalent to an activation energy of -13 ± 1.9 kJ mol^{-1} (95% confidence limits). The plot for log ΔE shows a change in slope at $1/T \sim 3.8 \times 10^{-3}$ K^{-1} ($\sim -7°C$). This temperature may be considered as the transition temperature of the process underlying the decrease of the elastic modulus of the viscous component. Below this temperature log ΔE is constant at a level of 9.39 ± 0.048, which is equivalent to

Figure 3 Experimental ($E(0)$) and initial (E_0) fibre modulus *versus* temperature
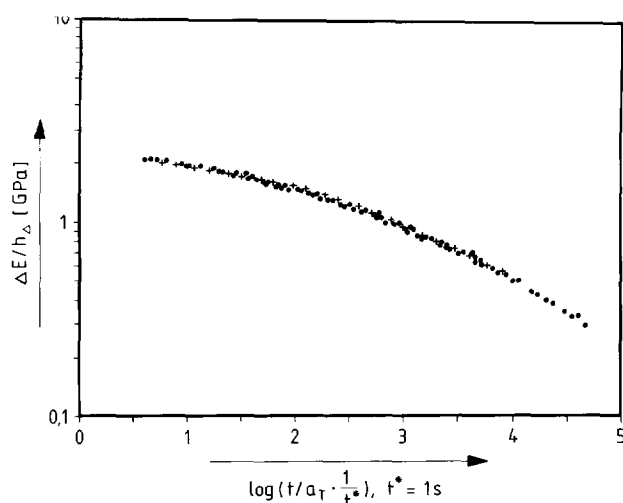
Figure 6 Mastercurve for the relaxation modulus of the viscous phase for a reference temperature of -47 C. The data for the reference curve are shown by crosses ($+$)
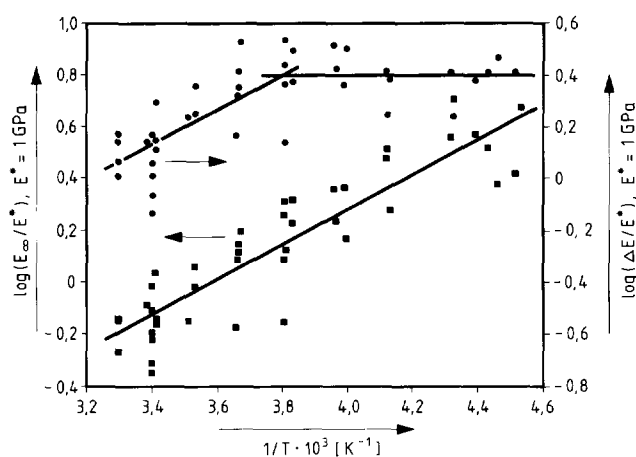

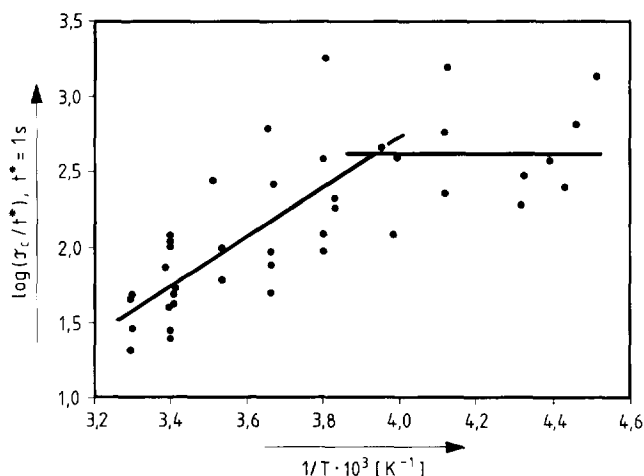**Figure 7** The moduli of the TC model presented as Arrhenius plots

Figure 8 The characteristic relaxation time (as log τ_c) presented as an Arrhenius plot

$\Delta E = 2.45$ GPa. Above the transition temperature, log ΔE decreases along a straight line, the slope of which is compatible with that of log E_x, as realized in *Figure 7*, so that the temperature dependence of both moduli relates to the same activation energy.

Although the initial investigation[21] showed basically a linear relationship for log τ_c in the Arrhenius diagram for the whole temperature range, with an activation energy of -20 kJ mol^{-1}, a closer examination, including further measurements, indicates, as realized in *Figure 8*, a discontinuity at around $1/T = 3.9 \times 10^{-3}$ K^{-1} ($-17°C$), where log τ_c stays constant below this onset temperature at a level of 2.6 ± 0.2, equivalent to a mean relaxation time of 400 s. Above $-17°C$, log τ_c decreases linearly with $1/T$, with an activation energy of -31 ± 13 kJ mol^{-1}, in reasonable agreement with the previous estimate[21], and at least of the same order as the activation energies for the moduli.

In view of the scatter in log ΔE, as well as in log τ_c on the $1/T$ scale, the transition temperatures for both parameters can be considered as being equal, occurring at approximately $-15°C$ $(1/T \sim 3.85 \times 10^{-3}$ K^{-1}). Although ΔE and τ_c follow Arrhenius relationships beyond the transition temperature, the data do not exclude the possibility that for a wider temperature range a change towards a Williams–Landel–Ferry-[22], or similarly, a Vogel–Fulcher-[23,24] type behaviour might be observed.

DISCUSSION

In view of the formal structure of the TC model and of the frequently proposed two-phase structure of semi-crystalline polymers it appears plausible, at least on a qualitative basis, to link the change of E_x with temperature to the change of the modulus of the crystallites in isotactic polypropylene. Nakamae *et al.*[16] investigated, by means of X-ray diffraction, the temperature dependence of the elastic moduli of the crystalline regions of isotactic polypropylene, in the direction parallel (E_l) and perpendicular (E_t) to the chain axis. While E_l was temperature independent up to $\sim 100°C$, E_t showed a pronounced temperature dependence (see Figure 12 in ref. 16) which can be shown to largely follow an Arrhenius relationship, with an activation energy of -7 ± 2.3 kJ mol^{-1}. The value for the activation energy of E_t is close enough to the activation energy found for E_x to allow us to argue in favour of an interrelationship between the two parameters. However, the differences also emphasize the decisive role of other factors, such as the arrangement of crystallites, orientation, etc.[5,15], which contribute towards the effective value of E_x and its change with temperature.

The activation energies obtained here are small when compared with the literature data[6,14,18] and also to the value we obtained by applying the TRS principle to our curves[21]. The TRS values always range (unrealistically high[19]) at around 150–200 kJ mol^{-1} and are thus about one order of magnitude higher than those obtained by the TC model. Rather, the low activation energies found here seem to identify the process as a simple non-cooperative relaxation process and, furthermore, show good agreement with the cohesive energy of ~ 20 kJ mol^{-1}, obtained for both propene and propane[25].

To identify the type of relaxation process, measurements of the tensile, dynamic mechanical properties at constant frequency (2 Hz), and for a temperature range between -100 and $+100°C$, were conducted, and the tan δ results are shown in *Figure 9*. The curve reveals two, well
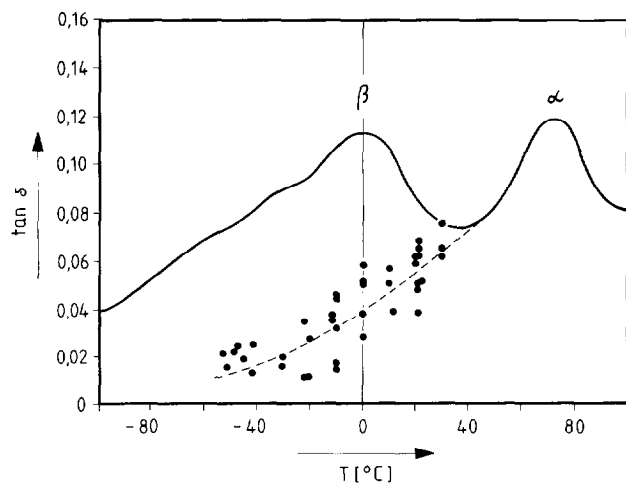
Figure 9 Tan δ as a function of temperature, obtained from a dynamic mechanical, extensional test at 2 Hz (solid curve) and the data obtained on the basis of the individual parameter values in *Figures 4* and *5* by applying equation (11) (●); the peaks are identified as the α- and β-transitions
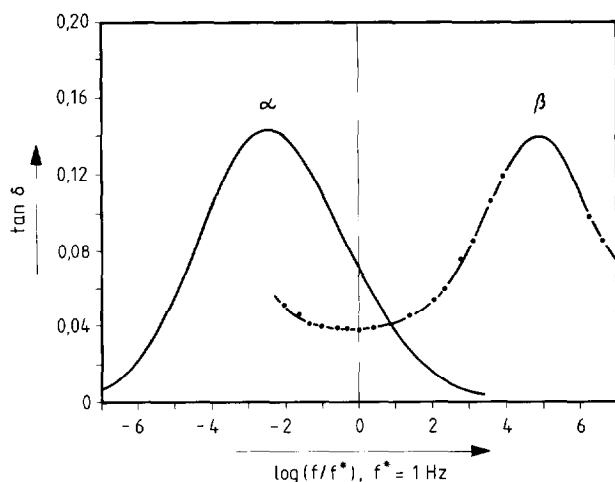

Figure 10 Variation in tan δ over the frequency range of the β-transition (—●—) with data taken from ref. 14, and calculated for the α-transition on the basis of the theoretical values of the parameters in *Figures 7* and *8* (—) for 30°C

separated transitions with maxima at $\sim -5°C$ and $\sim 70°C$, which are similar in shape, and can be identified as the β- and the α-transition, respectively[5].

The β-relaxation process is usually assumed to relate to the bulk amorphous phase, which is associated with the main glass transition temperature, while the α-process involves motion of the restrained amorphous component in the vicinity of the crystals[26-28]. In contrast to the expectations from Struik's theory for semicrystalline polymers[28], the two amorphous components show, in this present case, well separated and similar, thermo-mechanical transitions.

Read *et al.*[26] investigated the static and dynamic creep performance of isotactic polypropylene at room temperature, between 10^{-7} and 10^5 s and found two processes (α and β) separated by approximately eight decades of time. Read[14], furthermore, investigated the dynamic mechanical properties of isotactic polypropylene specimens, determining E' and E'' over the frequency domain from 10^{-2} to 10^6 Hz at various temperatures

between -10 and $+50°C$. The data for 30°C were taken from ref. 14, values for tan δ ($= E''/E'$) were calculated, and the results plotted in *Figure 10*.

By taking values of the parameters for the TC model for this temperature from the Arrhenius plots (see *Figures 7* and *8*), tan δ was calculated for the appropriate frequency range by using the following[28]:

$$\tan \delta(\omega) = -\pi/2 \, \text{dlog} \, E(t)/\text{dlog} \, t|_{\omega = 1/t} \qquad (11)$$

and are plotted together with Read's data for the β-process in *Figure 10*.

Read's data dominate the high-frequency range, while the process investigated here lies in the lower-frequency range. The two processes are very similar with respect to intensity and shape, in accordance with the dynamic mechanical properties (see *Figure 9*), and are separated by approximately eight decades of time, in good agreement with Read's results[14] for the static creep processes. The results clearly demonstrate that the experimental curves in *Figure 1* reflect part of the α-relaxation process of isotactic polypropylene. The similarity between the α- and the β-processes in the frequency, as well as in the temperature domain, suggest that an analogous TC-model approach, comprising an elastic and a relaxing component, may also be valid for the β-process. The results certainly support the view that similar molecular mechanisms are responsible for the two processes, where the β-process resides in the amorphous bulk phase and the retarded α-process in the restricted component which forms the interface with the crystals. This view is supported by the observation of Unwin *et al.*[29], using dynamic mechanical testing, that the β-relaxation in isotactic polypropylene progressively vanishes with increasing draw ratio.

Arriving, therefore, in view of *Figure 10*, at a three-component model for semicrystalline polymers requires a further specification of the TC model. It is found that ΔE is always the intensity of the relaxation process under investigation, while E_r contains the contribution from the crystalline phase, as well as the limiting elastic modulus of further viscoelastic processes not yet activated. However, since the α-process is the high temperature viscoelastic process in the material, the initial morphological interpretation of the TC model, given above, can be assumed to hold.

To further check the consistency of the description of the α-process by the TC model, tan δ was calculated according to equation (11) on the basis of the individual values of the parameters in *Figures 4* and *5* for 2 Hz over the relevant temperature scale. The results are shown in *Figure 9*. They correlate very well with the experimental data, thus confirming that the process that was investigated for this particular time and temperature scale actually covers the low-temperature region of the α-process well below its tan δ peak, and in a range which in the dynamic mechanical analysis strongly overlaps with the β-process. On this temperature scale, the onset, i.e. the transition temperature of the α-process, which occurs at approximately $-15°C$ (see *Figures 7* and *8*), agrees satisfactorily with the temperature range where the tan δ peak for the β-process occurs, as well as with the glass transition of the material. It is, furthermore, about 80°C lower than the location of the α-transition peak maximum, which is usually associated with the

transition temperature. This difference raises questions with respect to the nature of the tan δ peak, and this is the subject of our current investigations.

CONCLUSIONS

Our results show that the TC model is well suited for systematically describing the temperature dependence of the relaxation performance of isotactic polypropylene fibres, with the latter representing a strongly semi-crystalline polymer. Pronounced temperature dependencies of the component moduli are detected, while the change of the characteristic relaxation time τ_c is comparatively moderate, indicating a non-cooperative relaxation mechanism. Dynamic mechanical measurements support the consistency of the analysis approach. On this basis, further investigations will be conducted for other semicrystalline polymers in which the principles of both thermorheologically simple or complex materials also fail to provide a safe basis for the prediction of the long-term mechanical performance.

ACKNOWLEDGEMENTS

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