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Thermomechanics of isotactic polypropylene between −67 and +140°C: investigation of the relaxation behaviour based on literature data

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Faucher investigated the stress relaxation behaviour of isotactic polypropylene at temperatures between −67 and 140°C and found that a master curve could be formed by applying the principles for thermorheologically simple (TRS) materials. Since a previous investigation by the authors has shown that the TRS principle fails to model the viscoelastic performance of isotactic polypropylene consistently, Faucher's data are reanalysed on the basis of a two-component model. Application of the model leads to a good fit of the experimental data. The component moduli as well as the characteristic relaxation time show pronounced temperature dependencies and three different transition temperatures between −27 and +28°C. In Arrhenius plots the parameter values follow sigmoidal curves that differ in intensity and position but show a similarity in their shape, indicating comparable distributions of activation energies underlying the transitions. The consistency of the results is checked against tan δ data from dynamic, extensional tests. The diversity of the responses of the model parameters to temperature is considered as a reason for the variability of the glass transition temperatures measured for isotactic polypropylene using different techniques.

(Keywords: isotactic polypropylene; stress relaxation; two-component model)

INTRODUCTION

To confidently apply polymeric materials for construction purposes detailed knowledge about their viscoelastic long-term performance is required. The usual method to acquire this information is to conduct short-term relaxation or creep tests at various temperatures with subsequent superposition of the curves to form a master curve over an extended temperature range, from which long-term predictions are made. The approach where the curves are superimposed only by horizontal shifts along the log (time) axis applies for 'thermorheologically simple' (TRS) materials[1] and apparently works well for a variety of polymers[2–4], although obvious difficulties with this approach are observed for semicrystalline polymers[5,6] which play an important role as construction polymers.

In a previous paper[7] the authors reported investigations on the relaxation behaviour of isotactic polypropylene fibres in the temperature range −50 to +30°C and at strains in the linear viscoelastic region ($\varepsilon < 2\%$). The results relate to the α-transition of the polymer, which morphologically is attributed to the restricted amorphous phase in the semicrystalline material. Following Ferry's[8] general approach the relaxation curves were analysed using a two-component (TC) model, containing an elastic modulus and a modulus/relaxation function combination. Application of the TC model revealed pronounced influences of the temperature on the moduli of the components and only moderate displacements of the relaxation function of the log(time) scale[7].

On conducting similar experiments on isotactic polypropylene samples, Faucher[9] previously found, for an even more extended temperature range (−67 to +140°C), that his relaxation curves could be superposed by strictly horizontal shifts on the log(time) scale, in this representing a TRS material. Since both analytical approaches cannot be equally valid for the same type of material, we applied the TRS principle to our relaxation curves[10] and checked the ensuing prediction for the dynamic mechanical properties, namely for tan δ, against experimental results. The investigation showed that the TRS principle is only an empirically successful data reduction system that does not adequately model the time–temperature superposition for semicrystalline polypropylene.

To finalize the check of the consistency of the analysis, we have taken the curves from Faucher's paper[9] and submitted them to an analysis using the TC model. This approach offers the special advantage that Faucher's data, due to the nature of his specimen, cover a considerably larger temperature range than our previous investigation on polypropylene fibres[7] (see *Figure 2C*). The results show that Faucher's curves are in fact well described by the TC model, giving actually a nearly complete view of the temperature range covered by the α-transition of isotactic polypropylene and providing the basis for a new approach to the description of the temperature dependence of the model parameters.

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DATA BASIS AND METHOD OF ANALYSIS

The curves in Figure 5 of ref. 9 were digitized at equidistant points along the log(time) axis to give a total of 26 points for each curve. These were subsequently submitted to an analysis using the TC model, to be described in general terms below. More details of the model and a discussion of its relation to other approaches are given in ref. 10. *Figure 1* gives a suitable selection of data covering the whole temperature range in a log(modulus) *versus* log(time) graph, and also shows as solid lines, the theoretical description by the TC model based on curve-specific parameter values.

Following Ferry's[8] general approach, the relaxation curves are analysed using a two component (TC) model:

$$E(t,T) = E_\infty(T) + \Delta E(T)\Psi(t,T) \qquad (1)$$

where $E_\infty(T)$ and $\Delta E(T)$ are the temperature-dependent, limiting elastic moduli of an elastic and viscoelastic component, respectively. From a morphological point of view E_∞ and ΔE are attributed to the elastic response of the crystalline and the amorphous phase, respectively, where in this special case the relaxation relates to the restricted amorphous material[7]. $\Psi(t)$ is the relaxation function.

$\Psi(\ln t)$ is described here by using the cumulative log-normal distribution (CLND) function[7] given for the natural log(time) scale by:

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

where τ_c is the characteristic relaxation time, $\ln \tau_c$ the mean, and z the standard deviation, of the underlying log-normal distribution. x is the integration variable on the ln(time) scale. $\Psi(\ln t)$ forms a strictly symmetrical, sigmoid curve which drops from unity to zero within a range of approximately $\ln \tau_c \pm 4z$. This type of curve is chosen in preference to the usually applied Kohlrausch–Williams–Watt function[11] due to its strict symmetry, which coincides with experimental observations by Kubat (e.g. see ref. 12).

Following the concepts developed in ref. 7, the constant, 'universal' value of $z = 4.5$ is introduced to describe the shape of the relaxation function. This restriction implies that a change in temperature affects all relaxation times in a way described by a temperature-dependent, multiplicative factor. This concept is also inherent to the theory of thermorheologically simple materials[1] and leads to a simplification of equation (1) as:

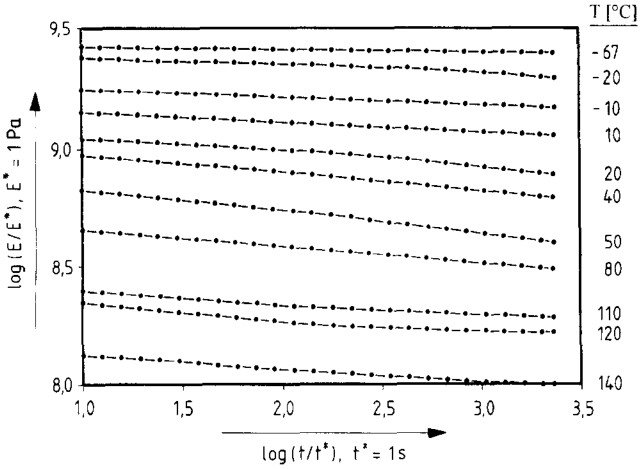

Figure 1 Representative set of log(relaxation modulus) *versus* log(time) curves for the temperature range investigated by Faucher[9]. The solid lines represent the theoretical fit through the data on the basis of the TC model

$$E(t,T) = E_\infty(T) + \Delta E(T)\Psi(t/a_T) \qquad (3)$$

where a_T is the acceleration factor, or as $\log a_T$ referred to as the shift factor, and is given by:

$$a_T = \tau_c(T)/\tau_c^R \qquad (4)$$

where τ_c^R is the characteristic relaxation time at the reference temperature. a_T is larger than unity for decelerated processes below, and smaller than unity for accelerated relaxations above the reference temperature. Log a_T consequently describes the displacement of the relaxation function on the log(time) scale to shorter times with increasing temperature.

In deviation from the fitting procedure described in detail in refs 7 and 13, using a weighted linear regression procedure, the combined equations (2) and (3) were directly fitted to the experimental data. We used the tanh approximation for $\Psi(\ln t)$ given in ref. 14, applied a least-squares criterion and made use of the non-linear optimization routine implemented in the spreadsheet program Quattro Pro (Borland).

Fitting the TC model to the individual relaxation curves given by Faucher in Figure 5 of ref. 9 for isotactic polypropylene specimens, the values for E_∞, ΔE and $\log \tau_c$ were determined for 18 temperatures between −67 and 140°C.

RESULTS AND DISCUSSION

The coincidence of the data points and the solid lines in *Figure 1* shows that the TC model leads to a good description of Faucher's relaxation curves.

Figure 2 summarizes the results for the model parameters in Arrhenius plots, to enable direct comparison with the results given in ref. 7. Following the line of reasoning of ref. 7, the temperature dependence of E_∞ is well described by a straight line in the Arrhenius plot over the whole temperature range (coefficient of determination $r_2 = 0.93$, see *Figure 2A*). From the slope of the line the activation energy is calculated as $E_A = -12 \pm 1.8\,\mathrm{kJ\,mol^{-1}}$ (95% confidence limits), in excellent agreement with the results of our previous investigation ($E_A = -13 \pm 1.9\,\mathrm{kJ\,mol^{-1}}$, ref. 7). In *Figure 2C* the temperature range investigated in ref. 7 is marked to indicate the increase in data range for which the initially proposed Arrhenius relationship for E_∞ still appears to be valid.

The values for ΔE reveal in Arrhenius plots (see *Figure 2B*) a similar behaviour as already observed for the fibres[7]. At low temperatures the values lie in an upper plateau range of $\log \Delta E = 8.9 \pm 0.09$ which is equivalent to $\Delta E = 0.81\,\mathrm{GPa}$. At $1/T = 3.32 \times 10^{-3}\,\mathrm{K^{-1}}$, equivalent to 28°C, a transition point is reached below which $\log \Delta E$ *versus* $1/T$ decreases along a straight line. For this line the same slope can be applied as for $\log E_\infty$ (see *Figure 2A*), so that again[7] equal activation energies are

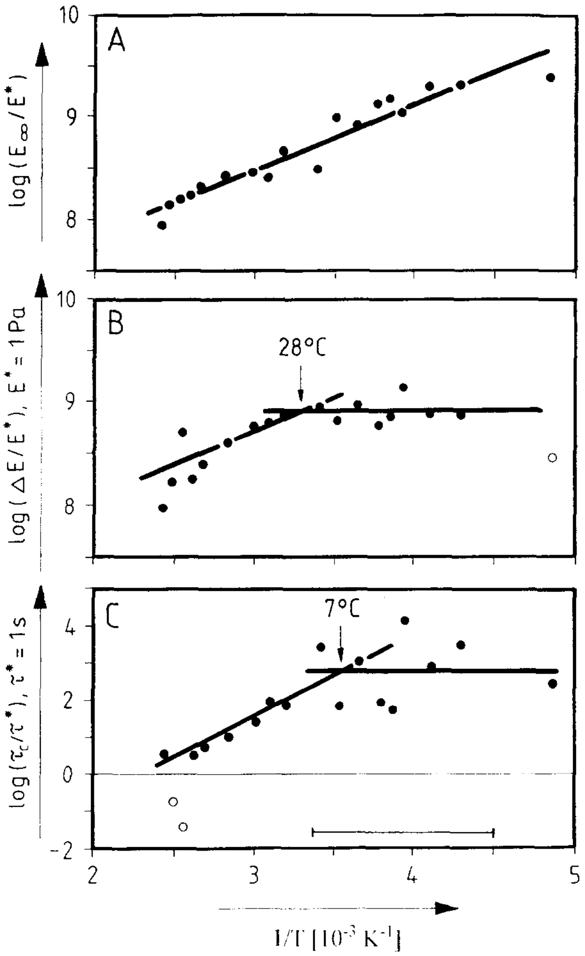

Figure 2 Values of the parameters of the TC model in Arrhenius diagrams with straight lines fitted through the data. Outliers are given as ○. The bar above the x-axis in (C) marks the temperature range investigated in ref. 7. The transition temperatures for ΔE and for τ_c are indicated

observed above the transition for the temperature dependencies of ΔE and E_∞.

Log τ_c shows a similar behaviour to ΔE. At low temperatures an upper plateau value of 2.7 ± 0.61 (≈ 560 s) is observed, which, below the transition point at $3.57 \times 10^{-3}\,\mathrm{K}^{-1}$, that is above 7°C, decreases linearly with a slope equivalent to $E_A = -40 \pm 17\,\mathrm{kJ\,mol}^{-1}$. The value for the upper plateau value for log τ_c as well as its activation energy are in satisfactory agreement with the previous results (log $\tau_c = 2.6 \pm 0.2$, $E_A = -31 \pm 13\,\mathrm{kJ\,mol}^{-1}$, ref. 7). The activation energies are for all parameters much smaller than those estimated on the basis of the TRS model ($150 \pm 20\,\mathrm{kJ\,mol}^{-1}$, ref. 10) and those given in the literature for log a_T (117 to $152\,\mathrm{kJ\,mol}^{-1}$, ref. 15).

The range of E_∞ values covering about 1.5 decades around 10^9 Pa is comparable to that for the fibres[7]. However, the upper plateau value for ΔE, 0.81 GPa, is considerably smaller than that previously found[7] (2.45 GPa); this may be attributed to a higher degree of crystallinity in Faucher's bulk samples compared with the fibres, which consequently lowers ΔE as the contribution of the amorphous component. This difference between the two types of sample coincides with the comparatively high transition temperatures for Faucher's polypropylene, namely for ΔE (28°C compared with −7°C for the fibres[7]) and for log τ_c (7°C compared with −17°C, ref. 7).

It is interesting to note that for both types of material the transition temperature for ΔE is roughly 10–20°C higher than that for log τ_c, despite the data scatter, so that a genuine difference between the two transition temperatures can be assumed, in this modifying the view expressed in ref. 7. Above 30°C all parameters are beyond their transition and decrease rapidly with temperature. This threshold agrees well with the temperature at which Struik[16] observed a change in the type of creep behaviour for polypropylene.

It follows from equation (3) that due to the temperature dependencies of E_∞ and ΔE, a master curve in the classical sense—that is by purely horizontal superposition on the log t scale—can only be realized for the relaxation function alone, which is given by:

$$\Psi(t/a_T) = [E(t/a_T, T) - E_\infty(T)]/\Delta E(T) \qquad (5)$$

The superposition of the $\Psi(t, T)$ data curves is realized in *Figure 3* for a reference temperature of 20°C and for the cases in *Figure 1* that cover the whole temperature range. The data points show good coincidence.

These results hence show that, as an alternative to the TRS method, Faucher's data can consistently be analysed using the TC model, yielding similar temperature dependencies of the model parameters as for the fibres[7]. The observed differences can be plausibly interpreted in terms of the structural differences of the materials.

To check the consistency of the approach, a dynamic mechanical property, namely tan δ, is calculated from the individual static relaxation curves using the approximation[16]:

$$\tan\delta(\omega) = -\pi/2\ \mathrm{d}\log[E(t)]/\mathrm{d}\log(t)|_{t=1/\omega} \qquad (6)$$

where ω is the frequency.

Figure 4 gives the tan δ values determined experimentally[7] for the fibres at a frequency of 2 Hz (●). The curve shows two maxima of similar shape and intensity at ∼ −5 and ∼ 70°C that are attributed to transitions of the amorphous (β-transition) and restricted amorphous (α-transition) phase in the material[5,7,17], respectively.

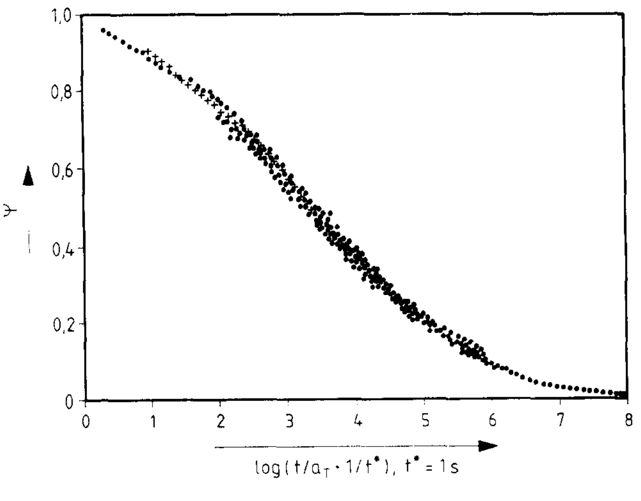

Figure 3 Master curve for the relaxation function, calculated from the data in *Figure 1* according to equation (5), and for a reference temperature of 20°C. The data for the reference curve are given as +

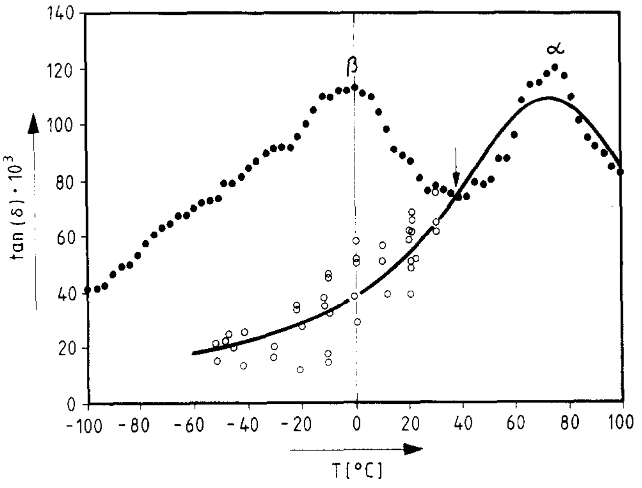

Figure 4 Tan δ data for the fibres at 2 Hz (●) and as obtained from the static relaxation curves (○) (for details see ref. 7). The arrow marks the minimum in tan δ between the α- and the β-transition at 39°C. The solid curve (——) gives the Lorentzian distribution for the α-relaxation peak with the parameter values given in *Table 2*

Figures 5A and *B* give as data points the tan δ values based on the individual, experimental parameter combinations of the TC model and calculated on this basis according to equation (6).

The solid line through the data in *Figure 5A* gives the tan δ values calculated by introducing the theoretical parameter values from the Arrnehius plots in *Figure 2*. The results show that this approach gives a seemingly adequate description of the data. It would predict an onset for the tan δ increase around 0°C and a continuous, slightly curved shape for the whole temperature range up to 200°C. This is certainly well beyond that point where a peak has to be expected from the experimental data in *Figure 2* and from the literature data in general[18]. However, the scatter of the data does not allow a decision on the true shape of the tan δ curve at the higher temperature end.

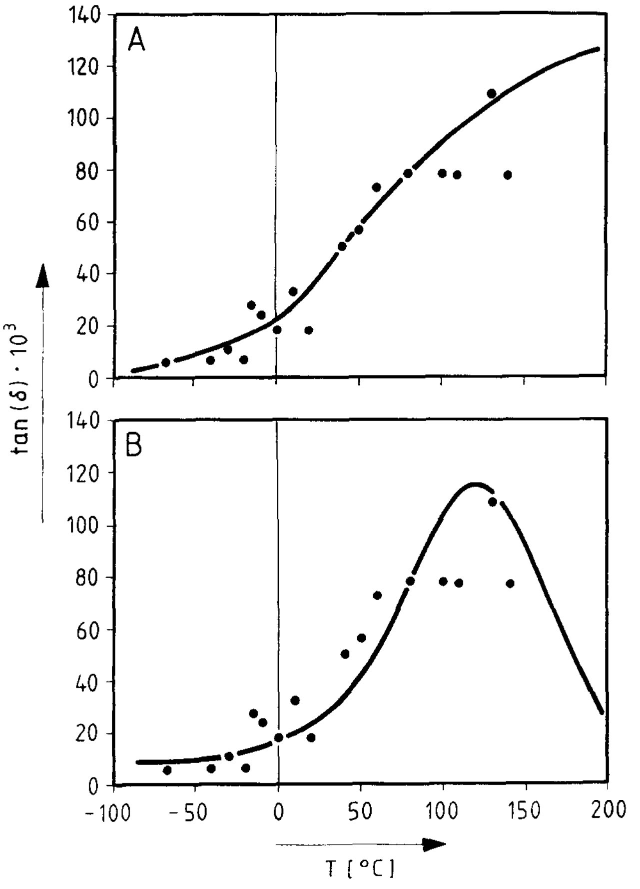

Figure 5 tan δ *versus* temperature (●) derived via equation (4) for a frequency of 2 Hz from the fit of the TC model to Faucher's[9] static relaxation curves. The solid lines are the theoretical curves derived on the basis of the straight-line fits in *Figure 2* (A) and of the sigmoid fits in *Figure 6* (B), respectively (see text)

The shortcoming of this parameter description to model a tan δ peak and to predict instead a continuous increase of tan δ even for unrealistically high temperatures, can be attributed to the large decrease predicted from the straight-line Arrhenius plots (see *Figure 2*) for the moduli and for the characteristic relaxation time at the high temperature end. This effect limits the plausibility of this parameter description to the region around the onset temperature for tan δ (*Figure 5A*).

A further refinement of the parameter description is based on the assumption that the initial descriptions in Arrhenius plots, using upper plateaux below and straight-line relationships above the transition temperature, is necessarily only an approximation for the real situation. A more realistic approach would imply that all three parameters undergo smooth, finite changes from an upper to a lower plateau value that start at their respective transition temperatures. This view agrees, for temperatures above the glass transition, with the general shapes of the Vogel–Fulcher[19,20] or Williams–Landel–Ferry[21] equations. The overall change is here assumed to be sigmoidal.

Applying the fitting procedures implemented in TableCurve (Jandel Scientific), sigmoid curves given by:

$$y = a + b/\{1 + \exp[-(x - c)/d]\} \qquad (7)$$

were fitted to the parameter values. y is the logarithm of the parameter of the TC model under consideration and $x = 1/T \times 10^3$ K. The parameters a and b in equation (7) give the lower level and the intensity of the process, respectively, so that the upper, low temperature level is given by $(a + b)$. c gives the position of the turnover point of the curve and d describes its width. The results of these fits are graphically summarized in *Figures 6A–C*. The parameters for the fits are given in *Table 1* together with their 95% confidence limits.

The results in *Table 1* show the intensity of the change of E_∞ with temperature, dropping from the upper plateau of $10^{(7.9+1.6)}$ Pa $= 3.2$ GPa by 1.6 decades to $10^{7.9} = 79$ MPa with a turnover point for the sigmoid curve at 30°C. The onset of the transition is estimated from *Figure 6A* at $1/T = 4.1 \times 10^{-3}\,\mathrm{K}^{-1}$, equivalent to −27°C.

Log ΔE shows a transition for which the intensity, given by an unrestricted fit of the sigmoid curve to the data, is not well defined, yielding an unrealistically high value of $b = 44.3$. A generally high intensity for the change in ΔE can be expected in view of the modulus or compliance changes at the glass transition for amorphous polypropylene[22] and for amorphous polymers in general. This is usually the order of 3–4 decades[3,4,8]. To stabilize the performance of the fit of the sigmoid curve to the data for log ΔE in *Figure 6B*, a restriction for the intensity to four decades ($b = 4$) was hence introduced.

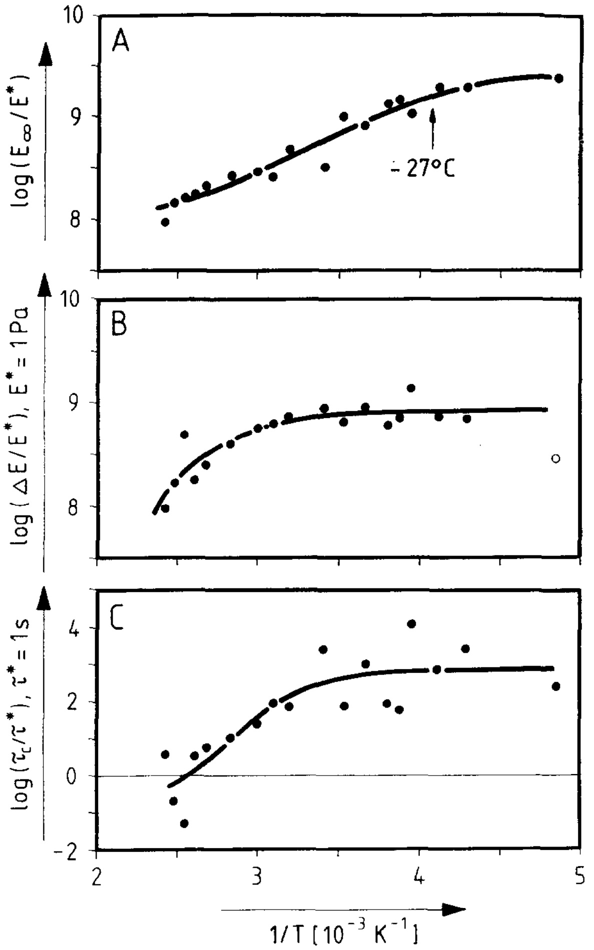

Figure 6 Values of the parameters of the TC model in Arrhenius diagrams. Sigmoid curves are fitted through the data for which the parameter values are given in *Table 1*. A data point considered as outlier is given as o. The arrow in (A) indicates the estimated transition temperature for E_∞

The results are given in *Table 1*. In view of the quality of the fit, it is important to note that the introduction of the restriction has only marginal influence on the form of the curve within the data range. On the basis of this fit, ΔE drops from an upper plateau value of $10^{(4.9+4)}$ Pa ≈ 800 MPa to $10^{4.9}$ Pa ≈ 80 kPa.

The sigmoid curve fit for log τ_c in *Figure 6C* basically models in a smooth way the results already obtained by the straight-line fits for the upper part of the transition (see *Figure 2B*). The sigmoid fit predicts a characteristic relaxation time of $10^{-0.8}$ s ≈ 0.2 s for conditions relating to the lower plateau, that is for the high temperature end of the transition. In view of the confidence limits (see *Table 1*) this prediction is in satisfactory agreement with the value of log $\tau_c = 1.8$ determined for the fibres at room temperature[13,23].

Table 1 Parameters for the sigmoid curves [equation (7)] fitted to E_∞, ΔE and τ_c, respectively, in the Arrhenius plots in *Figure 6*. For the meaning of the parameters and for the restriction of the fit for log ΔE, see text. r_2 = Coefficient of determination, ul = upper 95% confidence limit, 11 = lower 95% confidence limit

Parameter		log E_∞ $r^2 = 0.95$		log ΔE $r_2 = 0.81$		log τ_c $r^2 = 0.75$	
a	ul	7.9	8.5	4.9	5.1	−0.8	3.2
	ll		7.3		4.8		−4.7
b	ul	1.6	2.6	4	–	3.6	7.9
	ll		0.7		–		−0.7
c	ul	3.3	3.7	2.0	2.3	2.9	3.5
	ll		2.9		1.6		2.2
d	ul	0.5	0.9	0.3	0.6	0.2	0.7
	ll		0.1		0.1		−0.2

The estimates for the TC model parameters were taken from the sigmoid fits and introduced via equations (3) and (2) into equation (6). *Figure 5B* again gives the tan δ values derived from the experimental curves as data points and the solid line the theoretical values based on the sigmoid curve fits. A good fit to the data points is achieved, modelling a tan δ peak at 125°C. The intensity of the peak (≈ 0.11) is in good agreement with the peak maximum for the fibres (≈ 0.12, see *Figure 4*) and with literature data[18].

Though it is generally realized that the peak in tan δ does not signify a glass transition in a rigorous sense, it is nonetheless often used for this purpose[24]. For the present case of isotactic, semicrystalline polypropylene, none of the transition temperatures for the parameters of the TC model (E_∞, −27°C; ΔE, 28°C; log τ_c, 7°C) is related to the position of the α-transition peak for tan δ in *Figure 5B* (125°C). The peak thus does not signify a transition but only a combination of specific changes in the moduli and the characteristic relaxation time that lead to a maximum at a temperature that is in no obvious way related to the transition temperatures of the material.

To further emphasize the agreement between the double peak in the experimental data and the single peak derived from Faucher's data[9] for the static relaxation experiment, Sigma Plot (Jandel Scientific) was used to determine that the peak in *Figure 5B* is best described by a Lorentzian distribution given by:

$$y = e + f/\{1 + [(x - g)/h]^2\} \tag{8}$$

where $y = \tan\delta \times 10^3$ and $x = T/°\mathrm{C}$. The parameters e and f give the baseline level and the peak intensity, respectively, while g describes the peak position and h defines its width. The values for the parameters and their 95% confidence limits are given in *Table 2*.

To further the comparison the tan δ values for the dynamic mechanical experiment were taken for temperatures above the minimum between the α- and the β-process (39°C, indicated by the arrow in *Figure 4*) and combined with the tan δ data derived from the static relaxation curves for the fibres[7] (o in *Figure 4*). To this data pool a Lorentzian peak was fitted, given by the solid line through the α-transition data in *Figure 4*, for which the parameter values are given in *Table 2*.

Figure 4 shows that the data are well described by the Lorentzian distribution. The comparison of the parameter values in *Table 2* with respect to intensity (f) and width (h) furthermore shows that the peak shapes and intensities are in good agreement for the two cases (see *Figures 4* and *5B*). This leads us to conclude that the description of the tan δ data derived from Faucher's data is consistent with the experimental evidence, and that thus the general sigmoid description of the parameters of the TC model in Arrhenius plots exhibits a high degree of plausibility.

Table 2 Parameter values for the Lorentzian distributions [equation (8)] fitted to tan δ data in *Figure 4* (solid line) and *Figure 5B* with their confidence limits. Due to the virtual coincidence of the distribution and the tan δ curve in *Figure 5B* over most of the data range, no separate curve is given in this case. Definitions for r^2, ul and ll as in *Table 1*

Parameter		*Figure 4* $r^2 = 0.93$		*Figure 5B* $r^2 = 0.99$	
e	ul	6.6	15.7	−1.4	3.2
	ll		−2.5		−6.1
f	ul	102.5	111.1	119.8	125.9
	ll		93.9		113.7
g	ul	72.4	76.1	118.8	116.5
	ll		68.8		121.0
h	ul	48.5	57.7	51.7	57.0
	ll		39.2		46.4

CONCLUSIONS

The objective of this investigation was to solve the contradiction between the seemingly successful application of the TRS principle for polypropylene by Faucher[9] and our observation of the lack of validity of the TRS principle for this material[7]. It is shown that Faucher's data are in fact well described by the alternative TC model, leading to estimates for the dynamic mechanical properties that go beyond the previously considered temperature range and are in good agreement with experiments.

The analysis of the results indicates furthermore that the three parameters of the TC model—namely E_∞ and ΔE, considered as the elastic moduli of the crystalline and the restricted, amorphous fraction, respectively, and $\log \tau_C$—have distinctly different transition temperatures in the range between -27 to 28°C. This can be related to the concept of multiple glass transitions in semicrystalline polymers[25]. The diversity of the responses to temperature may be considered as the reason for the variability of the glass transition temperatures measured for isotactic, semicrystalline polypropylene when using different techniques[15] and as one source of the controversy over the transition temperatures of semicrystalline polymers in general (e.g. ref. 25).

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