Polymer Vol. 37 No. 12, pp. 2471–2476, 1996

0032-3861/96/$15.00 + 0.00

Analysing the relaxation behaviour of poly(tetrafluoroethylene) in the α-transition region by applying a two-component model*

F.-J. Wortmann
Deutsches Wollforschungsinstitut, Veltmanplatz 8, D-52062 Aachen, Germany
(Received 5 July 1995)

Semicrystalline polymers play an important role as materials for engineering purposes. Such a polymer is poly(tetrafluoroethylene) (PTFE), for which Araki investigated the compressive relaxation behaviour at temperatures between 60 and 150°C and met major difficulties in achieving a satisfactory systemization of his curves when using the principles of thermorheologically simple materials. The objective of this study is to investigate whether an improved systemization can be achieved on the basis of a two-component (TC) model containing an elastic component and a viscous component corresponding to the crystalline phase and the restricted amorphous phase in PTFE, respectively. The properties of the components show pronounced temperature dependence characterized by three different transition temperatures and activation energy distributions. To check the consistency of the model approach, $\tan\delta$ was calculated on the basis of theoretical parameter values and compared with experimental data taken from the literature. Prediction and experiment agree to an extent where even the fine structure of the $\tan\delta$ peak for the α-transition is reproduced. The investigation thus shows that the compressive relaxation curves measured by Araki are consistently described by the TC model, leading to the detection and description of three individual transitions that govern the overall viscoelastic performance of PTFE in the α-transition region. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(tetrafluoroethylene); compressive stress relaxation; time–temperature superposition)

INTRODUCTION

Semicrystalline polymers play an important role as materials for engineering purposes, and it is thus that an in-depth understanding of their viscoelastic performance and hence of their long term performance is of principal importance. However, the viscoelastic performance of semicrystalline polymers is generally considered as not being very well understood[1].

In a series of papers[2–6], the author and Schulz proposed a two-component (TC) model to systemize the relaxation performance of semicrystalline isotactic polypropylene. It was shown that the application of this model leads to a consistent analysis of the temperature dependent viscoelastic performance of this polymer[2,4], and in this exhibits major advantages over the application of the principles of thermorheologically simple (TRS) materials[3].

A polymer of major engineering importance is poly(tetrafluoroethylene) (PTFE), owing to its high melting point, resistance against corrosive agents, non-adhesive properties and low coefficient of friction. The mechanical properties of PTFE have been intensively investigated, as reviewed by McCrum *et al.*[7].

Araki[8] investigated the compressive relaxation performance of PTFE at temperatures between 60 and 150°C, i.e. in the α-transition region[7]. He met major difficulties in achieving a satisfactory systemization of the relaxation curves, namely their superposition on the basis of the TRS principles, and thus in providing a reliable basis for the prediction of the long term viscoelastic performance of the material. More favourable experiences with the application of the TRS principles for PTFE are reported by Nagamatsu and coworkers[9,10] and others[11,12].

To check whether an improved systemization of the viscoelastic performance could be achieved on the basis of the TC model, the relaxation curves from Araki's paper for a sample with 59% crystallinity were digitized and the resulting data reanalysed, as already exercised on literature data for polypropylene[4]. A good fit of the data was obtained, revealing three different transitions for the parameters of the model and a prediction of the dynamic mechanical properties of PTFE that is consistent with literature data[13].

DATA AND MODEL APPROACH

Araki[8] investigated the stress relaxation of moulded cylindrical PTFE samples of various degrees of crystallinity in compression. He obtained relaxation moduli of the order of megapascals over a time range between approximately 2 s and 45 min. These are given for a sample with 59% crystallinity and for temperatures between 60 and 150°C in *Figure 2* of his paper[8]. In the

---

* Dedicated to Professor Helmut Zahn on the occasion of his 80th birthday

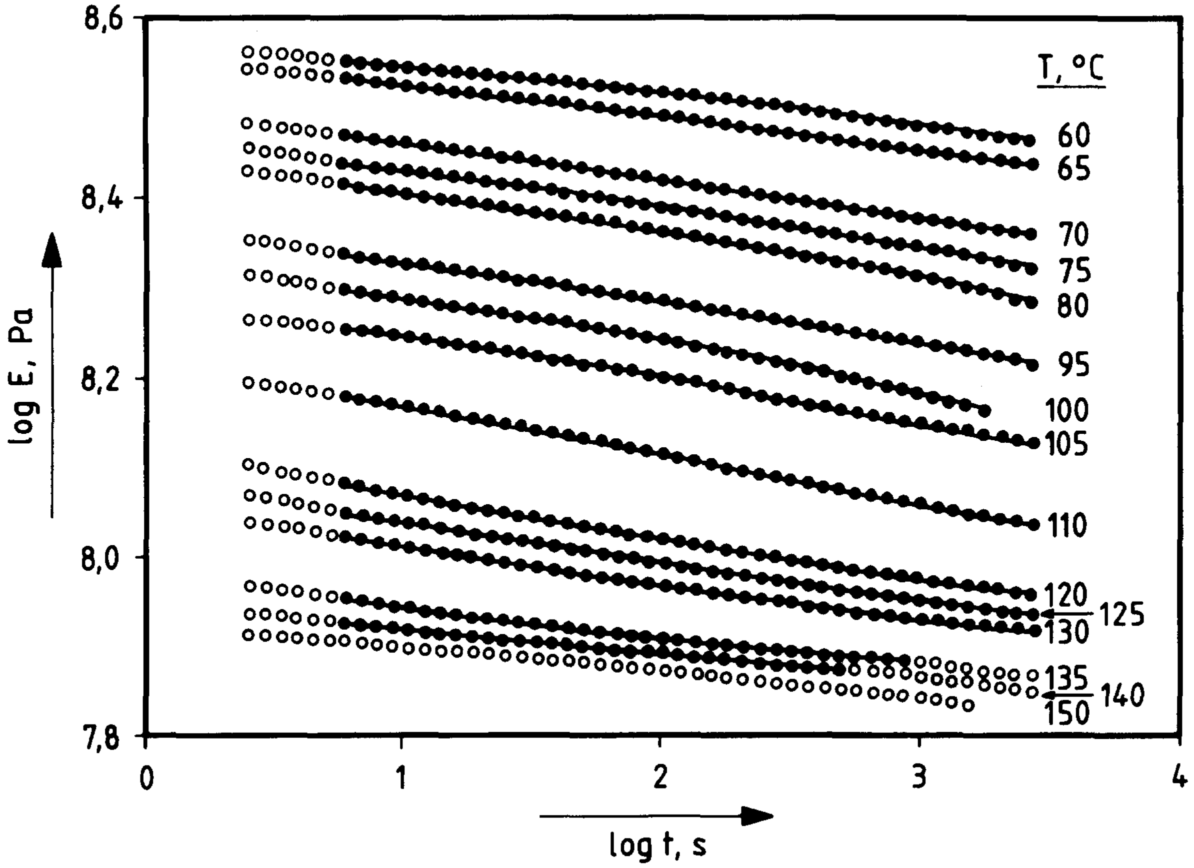

Figure 1 Compressive relaxation curves for PTFE given as log E vs. log t. The points relate to the digitized curves of *Figure 2* in the paper by Araki[8]. The solid lines represent the theoretical curve fits through the data on the basis of the individual parameter values for the TC model. The curves for 85, 90 and 115°C are omitted for reasons of clarity. The limits for the accepted data range are indicated by using open (not accepted) and filled (accepted) circles for the points

terminology introduced by McCrum *et al.*[7], this temperature range relates to that of the α-transition in PTFE.

The curves were digitized at 50 equidistant places on the x axis (log t axis) and transformed into the respective values of modulus in pascals and time in seconds. These data, given as a log E vs. log t plot in *Figure 1*, are the basis of the analysis of the relaxation behaviour using the TC model, as described below.

The first point is located at 2 s. For short times of up to about 6 s ($\log t = 0.78$), the curves at lower temperatures especially show a pronounced upward curvature in the modulus vs. log t plot, indicating influences of the short time and low temperature β-process. To avoid these effects, we omitted data for $t < 6$ s. The short time restriction is indicated in *Figure 1*.

Owing to the onset of a further relaxation at longer times and for temperatures above 130°C, restrictions had to be introduced for the long time range of the higher temperature curves. The individual upper limits that were imposed are indicated for the curves in *Figure 1*. For the relaxation curve at 150°C, the long term process appears to have merged with the process under consideration, preventing the analysis. The need for the introduction of upper time limits for temperatures beyond 130°C coincides with McCrum's[13] observation for the torsional modulus that the α-process ends in this temperature range and leads towards the melting transition.

The data are analysed, as previously described in detail for polypropylene (PP)[2,4], by applying a two-component (TC) model of the form

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

where $E_{\infty}(T)$ and $\Delta E(T)$ are the temperature dependent limiting elastic moduli of an elastic and a viscous component, respectively, and $\Psi(t,T)$ is the temperature dependent relaxation function.

From a morphological point of view, and in a similar way as for PP[2,4], the modulus parameters of the TC model are interpreted on the basis of a structural two-phase model for PTFE composed of a crystalline and an amorphous phase[14].

Here, $\Psi(\log t)$ is described using the cumulative log-normal distribution (CLND) function given for the log t scale by

$$\Psi(\log t) = 1/[(2\pi)^{1/2}z]\int_{\log t}^{+\infty} \exp\{-\tfrac{1}{2}[(x-\log\tau_c)/z]^2\}\,dx \qquad (2)$$

where τ_c is the characteristic relaxation time, $\log\tau_c$ the mean and z the standard deviation of the underlying log-normal distribution. Here, x is the integration variable on the log t scale. The function $\Psi(\log t)$ forms a strictly symmetrical sigmoid curve which drops from 1 to 0 within a range of approximately $\log\tau_c \pm 4z$. From a formal point of view, equation (1) for stress relaxation is equivalent to the description given by Schapery for the creep of a so-called thermorheologically complex material of type 2 (TCM-2)[15].

Attempts were made to fit equations (1) and (2) to the data without any restriction, making use of the tanh approximation for $\Psi(\log t)$ given elsewhere[16], and applying the non-linear optimization routine implemented in the program Quattro Pro (Borland). However, the results showed pronounced instabilities of the fit, originating mainly from the low resolution of the data source. In a similar way as for the analysis of the literature data for PP[4] and from the concepts developed elsewhere[2], the constant 'universal' value for z of 1.95, equivalent to $z = 4.5$ for the $\ln t$ scale, was introduced to describe the shape of the relaxation function. This restriction implies, for example, that a change in temperature affects all relaxation times in a way that is described by a temperature dependent multiplicative factor. This assumption is also inherent to the theory of thermorheologically simple (TRS) materials[1] and leads to a simplification of equation (1) as

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

where a_T is the acceleration factor, or as $\log a_T$ is 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 mean relaxation time at a reference temperature.

It is interesting to note that the assumed constancy of the shape of the relaxation function through the temperature range of the α-relaxation corresponds to the observations by Connolly *et al.*[17] on the dielectric behaviour of substituted poly(p-phenylenes).

The combination of equations (2) and (3) with the *a priori* restriction applying to z could stably be fitted to the experimental data for the compressive relaxation curves of PTFE[8], yielding the individual values for E_∞, ΔE and $\log \tau_c$ for 18 temperatures between 60 and 150°C.

RESULTS AND DISCUSSION

Figure 1 gives the relaxation data in a $\log E$ vs. $\log t$ plot for ease of presentation, and the curves fitted through them for the accepted data range. The curves were calculated on the basis of the TC model using the individual curve specific sets of parameter values. Good fits were achieved in all cases.

To elucidate the temperature dependence of the parameters, we plotted them in so-called Arrhenius diagrams (*Figures 2a–c*), first for the viscous component and then for the elastic component.

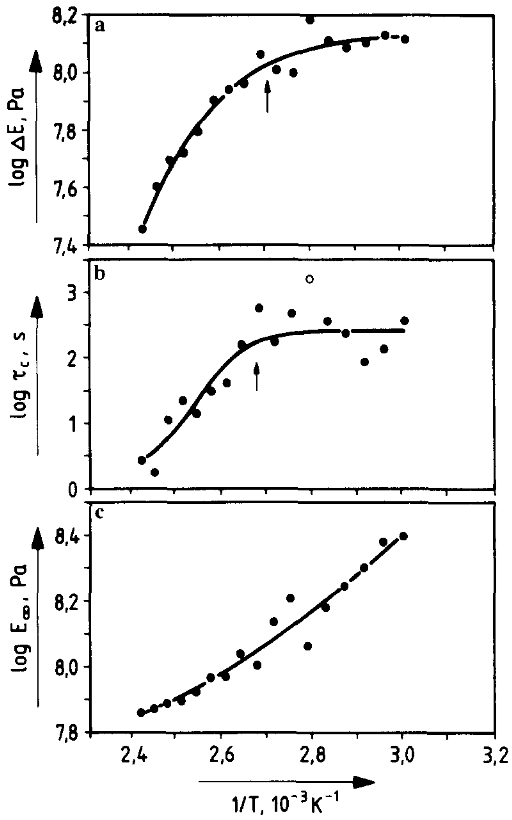

Figure 2 Values of the parameters of the TC model in Arrhenius plots: (A) ΔE, (B) τ_c and (C) E_∞. Sigmoid curves (solid lines), for which the parameter values are given in *Table 1*, are fitted through the data. A point considered as an outlier is given as an open circle. The arrows indicate the estimated onset temperatures of the transitions

Table 1 Parameter values and standard errors (*SE*) *of the sigmoid fits for the Arrhenius plots in Figure 2* (see equation (5)). The coefficients of determination (r^2) and the characteristic temperatures (T_{on} = onset temperature, T_{tr} = transition temperature) are also given

Parameter	ΔE	E_∞	τ_c
a	5.7	7.5	0.2
SE	4.7	1.1	0.6
b	2.4	2.8	2.2
SE	4.8	19.5	0.7
c	2.3	3.4	2.5
SE	0.4	5.0	0.04
d	0.13	0.5	0.06
SE	0.06	1.5	0.03
r^2	0.97	0.95	0.88
T_{on} (°C)	100	−60	100
T_{tr} (°C)	163	24	120

The previous investigation of PP[4] showed the advantages of using sigmoid fits in the Arrhenius plot to arrive at a satisfactory prediction of the dynamic mechanical properties. The sigmoid curve is given by

$$y = a + b/\{1 + \exp[-(x - c)/d]\} \qquad (5)$$

where 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 (5) give the lower level and the intensity of the process, respectively. The upper low temperature level is hence given by $(a + b)$. Here, c gives the position of the turnover point of the curve and d describes its width. The results of the curve fits are given as solid curves in *Figures 2a–c*, for which the parameters are summarized in *Table 1* together with their standard errors, their coefficients of determination (r^2) and the characteristic temperatures of the transitions.

The results for the elastic limiting modulus of the viscous component (ΔE) are fitted well by the sigmoid curve ($r^2 = 0.97$, see *Table 1*). ΔE decreases from an upper level of 132 MPa ($= 10^{8.1}$ Pa) by approximately 2.5 orders of magnitude to a lower level of 490 kPa ($= 10^{5.7}$ Pa). Such a decrease is generally consistent with the modulus change to be expected for an amorphous crosslinked polymer at the glass transition. The lower level is a rather rough estimate, considering its standard error, owing to the fact that it is well outside the experimental range. This level for ΔE is expected to be reached at temperatures beyond about 250°C ($1/T \approx 1.0 \times 10^{-3}\,\mathrm{K}^{-1}$). The onset temperature is estimated, as indicated in *Figure 2a*, at about 100°C ($1/T \approx 2.7 \times 10^{-3}\,\mathrm{K}^{-1}$). In modifying the view expressed elsewhere for PP, we take the transition temperature as the inflection point of the curve, which is given by the parameter c (see *Table 1*) at 163°C ($1/T = 2.3 \times 10^{-3}\,\mathrm{K}^{-1}$).

The shape parameter of the transition, $d = 0.13$, agrees, in view of its standard error, reasonably well with the value determined for the analogous transition in polypropylene[4] ($d = 0.3$).

The change in $\log \tau_c$ in the Arrhenius plot is also well described by a sigmoid curve ($r^2 = 0.88$). The characteristic relaxation time starts off at a rather low level of $\log \tau_c = 2.4$ (about 260 s) and decreases by 2.2 orders of magnitude beyond an estimated onset temperature of 100°C to a lower level of 0.2 (about 1.6 s), indicating a fast relaxation process. The inflection, i.e. the transition temperature, is at 120°C. It is interesting to note that both ΔE and τ_c, assumed to originate from the amorphous component in PTFE, show onset and transition temperatures that cover the range in which by dilatometry and X-ray diffraction at 130°C a transition is observed for the amorphous phase[18].

The shape of the sigmoid curve for $\log \tau_c$, given by $d = 0.06$ (see *Table 1*), again agrees well with the results for polypropylene[4]. Furthermore, the agreement in the shape factor for the transition in $\log \tau_c$ is not the only coincidence between the properties of PTFE and PP. Good agreement is also observed for the upper (PTFE, 2.4; PP, 2.8) and lower (PTFE, 0.2; PP, −0.8) levels of $\log \tau_c$.

The unrestricted fit of the sigmoid curve for the elastic component E_∞ reveals that the points only cover a narrow range of the lower part of the curve. Though the quality of the fit in the data range is very satisfactory ($r^2 = 0.95$), the values for most of the parameters are accompanied by large standard errors (see *Table 1*), so that appropriate care has to be taken with their interpretation.

According to the fit, the upper limit value for E_∞ is 22 GPa ($10^{10.35}$ Pa), which is reached at temperatures below approximately −60°C. This upper limit of the modulus is in adequate agreement with the related value for PP[4] ($10^{9.5}$ Pa), and can thus be considered as reasonable. The modulus drops by 2.8 orders of magnitude to a low level of 0.6 kPa ($10^{2.8}$ Pa), which is reached at temperatures above approximately 260°C. This temperature agrees with the upper service temperature of PTFE[19] (260°C) and approaches the crystalline melting point at 327°C. On the assumption that E_∞ originates in the crystalline phase of the polymer, this change is rather large compared, for example, to the analogous change for polypropylene[4] (about 1.6 decades). However, in view of the fact that the turnover point of the sigmoid curve in *Figure 2c* at 24°C coincides with the temperature range for which in the literature[20] are described first-order transitions from a more to a less ordered crystal structure for PTFE (19°C, 30°C), the large change in E_∞ is understandable. It is interesting to note that the shape factor of the sigmoid curve, $d = 0.5$, agrees well with the corresponding value for polypropylene[4] ($d = 0.5$).

It is thus that for all three parameters of the TC model, agreement in the shapes of the sigmoid transitions in the Arrhenius plots with those for polypropylene[4] is observed, which may indicate a certain material invariance of the nature of these transitions for semicrystalline polymers, which corresponds to an invariance of the shape of the relaxation function.

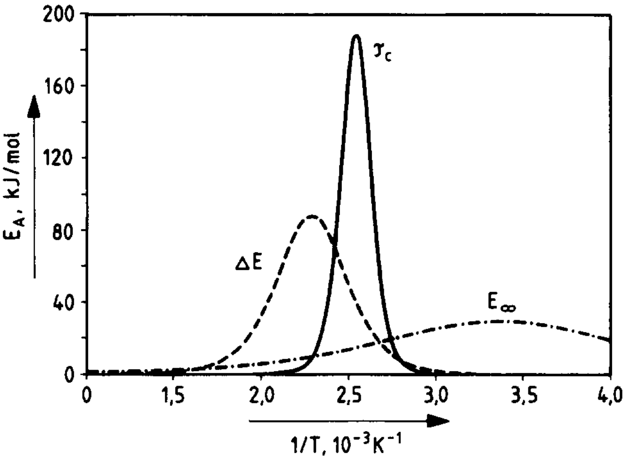

Figure 3 Distributions of activation energies for the parameters of the TC model as derived from the sigmoid curve fits of the Arrhenius plots in *Figure 2*

The fit of the sigmoid curves (*Figures 2a–c*) implies, on the basis of the Arrhenius equation

$$y = A \exp(E_A/RT) \tag{6}$$

that the process is controlled by a distribution of activation energies. Here, y is the parameter under consideration, A the pre-exponential factor, i.e. the value of y at infinite temperature, and E_A the activation energy. The distributions of E_A were calculated in the usual way on the basis of the first derivatives of the curves in *Figure 2*, and are presented in *Figure 3*. Owing to the fact that a sigmoid curve is a good approximation for a cumulative normal distribution, the activation energies are basically normally distributed on the $1/T$ scale.

The shapes and maxima of the distributions are quite different for the three parameters, reaching 29, 88 and 190 kJ mol^{-1} for E_∞, ΔE and τ_c, respectively. The maxima are substantially higher than those that may be estimated on the basis of simple straight line fits for the experimental data range, where, however, the absolute values of maximum E_A for all parameters are still well below those estimated on the basis of the TRS principle[7,8] (around 500–1000 kJ mol^{-1}).

To investigate the validity of the application of the TC model and the descriptions for the temperature dependence of the parameters, as for PP[2,4], we checked the prediction of the dynamic mechanical performance, namely of $\tan \delta$, for its consistency with experimental data.

McCrum[13] investigated by the free torsional oscillation method the damping performance of PTFE sheets of various degrees of crystallinity in the temperature range 4–600 K (−269 to 327°C). The two curves for crystallinities comparable to Araki's[8] sample (59%) and for the relevant temperature range of 50–250°C are given in *Figure 4a*. Since McCrum's curves are given in terms of the logarithmic decrement Λ, $\tan \delta$ is calculated according to[21]

$$\tan \delta_T = \Lambda/\pi \tag{7}$$

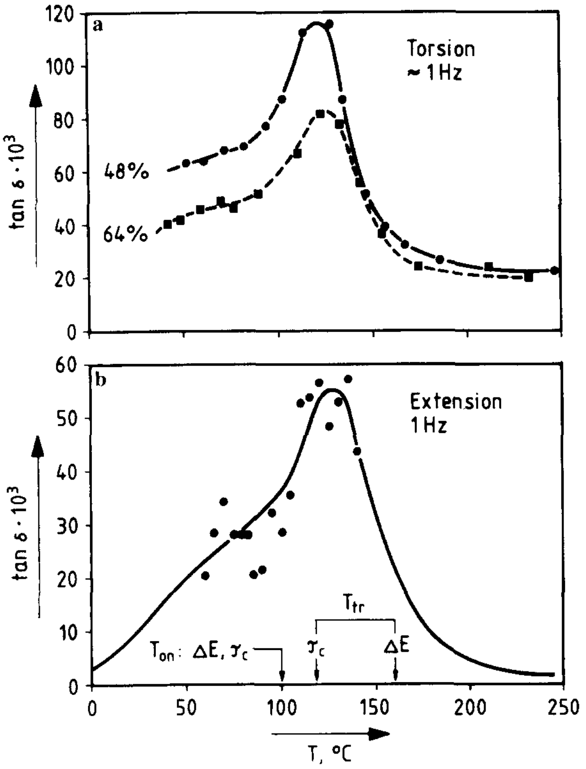

Figure 4 (a) Experimental $\tan\delta$ data from torsion experiments on PTFE samples of two degrees of crystallinity (as indicated) from McCrum[13]. (b) The $\tan\delta$ values (points) deduced from the individual curve fits of the TC model to the static relaxation curves via equation (8) and the $\tan\delta$ prediction (solid line) based on the sigmoid curve fits of the Arrhenius plots (see *Figure 2*). The various onset and transition temperatures for the parameters are indicated. The y scales for (a) and (b) differ by a factor of two for reasons of clarity

where the subscript T indicates that the parameter relates to a torsion experiment.

Figure 4a shows two single peaks for the α-transition located at 126°C (48% crystallinity, 0.62 Hz) and at 128°C (64% crystallinity, 0.98 Hz), respectively, that are well separated from the transitions at lower temperatures. Owing to its decrease in intensity with increase in crystallinity, this α-process has been attributed to the amorphous phase in PTFE[13]. Although this has been questioned[22], further studies by Satokawa and Koizumi[18], using dilatometry and X-ray diffraction, support this view. In view of the similarities between the $\tan\delta$ spectra of PTFE[7] and PP[2,4], showing two adjacent peaks of comparable spacing, we attribute the α-relaxation of PTFE to the restricted amorphous phase. It is interesting to note that both $\tan\delta$ curves in *Figure 4a* exhibit a further shallow peak or shoulder around 70°C assumed to be part of the β-process[7].

Introducing the individual values for the parameters of the TC model, as given by the points in *Figure 2*, into equations (2) and (3), we can calculate $\tan\delta$ for a given frequency ω according to[23]

$$\tan\delta_{\mathrm{E}}(\omega) = -(\pi/2)\,\mathrm{d}\log E/\mathrm{d}\log t\big|_{t=1/\omega} \qquad (8)$$

where the subscript E for $\tan\delta$ refers to extension. The individual results for $\omega = 1$ Hz are given in *Figure 4b*. Making use of the theoretical values for the parameters as derived from the sigmoid fits in *Figures 2a–c* leads to the solid curve for $\tan\delta$ in *Figure 4b*.

The theoretical $\tan\delta$ values form a peak that adequately describes the data that are derived from the experimental relaxation curves. The position and the shape of the peak coincide well with McCrum's[13] results. In view of the differences in the test geometries, the agreement between the absolute values of $\tan\delta$ is considered as satisfactory. It is interesting to note that the peak in *Figure 4b* is not symmetrical but also reproduces the experimentally observed low temperature shoulder between 50 and 100°C, usually attributed to the β-transition in PTFE[7].

Consideration of the various characteristic temperatures indicated in *Figure 4b* (see also *Table 1*) reveals how the shape and the shape changes of the $\tan\delta$ curve are related to the transitions of the viscous component of the TC model. The shoulder between 50 and 100°C is actually the expression of the onset temperatures of the transitions in ΔE and τ_c. The peak itself is only controlled by the transition in the characteristic relaxation time. The transition temperatures for τ_c (120°C) and ΔE (163°C) agree reasonably well with the two transitions, presumably of second order[8,24], that are observed in this temperature range[25].

It has thus to be concluded that the $\tan\delta$ peak does not signify a singular transition in PTFE or possibly a combination of the α-process and the β-process, but is rather the final result of the complex interaction of various transitions occurring in the material in the α-transition region.

As described in the literature[24,25], there are up to six transition temperatures or temperature ranges detected in PTFE by a wide variety of methods that can be attributed to first-order and second-order transitions. It will be the objective of further investigations to elucidate further the relationships between these transitions and the characteristic temperatures of the parameters of the TC model.

CONCLUSIONS

The static, compressive relaxation performance of semicrystalline PTFE in the region of the α-transition shows that the curves can be nicely systematized on the basis of the two-component model in a way that is consistent with the dynamic mechanical properties.

The temperature dependent performance of the parameters of the model, attributed to the crystalline phase and the restricted amorphous phase, reveals the characteristic and individual transition temperatures of the components, which are considered as one source of the controversy over the transition temperatures in PTFE.

REFERENCES

1 Schwarzl, F. R. 'Polymer-Mechanik', Springer, Berlin, 1990
2 Wortmann, F.-J. and Schulz, K. V. *Polymer* 1995, **36**, 315
3 Wortmann, F.-J. and Schulz, K. V. *Polymer* 1995, **36**, 1611
4 Wortmann, F.-J. and Schulz, K. V. *Polymer* 1996, **37**, 819
5 Wortmann, F.-J. and Schulz, K. V. *Polymer* 1994, **35**, 2108
6 Wortmann, F.-J. and Schulz, K. V. *Polymer* 1995, **36**, 2363
7 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967
8 Araki, Y. *J. Appl. Polym. Sci.* 1965, **9**, 1515
9 Nagamatsu, K. *Kolloid. Z.* 1960, **172**, 141

10 Nagamatsu, K., Yoshitomi, T. and Takemoto, T. *J. Colloid Polym. Sci.* 1958, **13**, 257

11 Cherskii, I. N., Kozyrev, V. A., Morov, V. A., Gerasimov, A. A. and Kovalenko, N. A. *Polym. Mech.* 1977, **13**, 623

12 Koo, G. P., Jones, E. D., Riddell, M. N. and O'Toole, J. L. *SPE J.* 1965, **21**, 1100

13 McCrum, N. G. *J. Polym. Sci.* 1959, **34**, 355

14 Davidson, T. and Gounder, R. N. *Polym. Sci. Technol. B* 1984, **12**, 775

15 Schapery, R. A. in 'Mechanics of Composite Materials' (Ed. G. P. Sendeckyi), Vol. 2, Academic Press, New York, 1974, p. 85

16 Wilrich, P.-Th. and Henning, H.-J. 'Graf, Henning, Stange, Wilrich: Formeln und Tabellen der Angewandten Mathematischen Statistik', Springer, Berlin, 1987

17 Connolly, M., Karasz, F. and Trimmer, M. *Macromolecules* 1995, **28**, 1872

18 Satokawa, T. and Koizumi, S. *J. Chem. Soc. Jpn, Ind. Chem. Sect.* 1962, **65**, 1211

19 Sperati, C. A. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 3rd Edn, Wiley, New York, 1989, p. V35

20 Sperati, C. A. and Starkweather Jr, H. W. *Fortschr. Hochpolym.-Forsch.* 1961, **2**, 465

21 Tobolsky, A. V. in 'Polymer Science and Materials' (Eds A. V. Tobolsky and H. F. Mark), Krieger, New York, 1980, Ch. 10

22 Ohzawa, Y. and Wada, Y. *Rep. Prog. Polym. Phys. (Jpn)* 1963, **6**, 147

23 Struik, L. C. E. *Polymer* 1987, **28**, 1521

24 Gangal, S. V. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. Mark, N. Bikales, C. Overberger and G. Menges), Vol. 16, Wiley, New York, 1989, p. 577

25 Lau, S.-F., Wesson, J. P. and Wunderlich, B. *Macromolecules* 1984, **17**, 1102