Polymer 40 (1999) 1611–1615

polymer

Polymer Communication

Modeling the dynamic performance of poly(tetrafluoro ethylene) in the α-transition region

F.-J. Wortmann

Deutsches Wollforschungsinstitut an der RWTH Aachen e.V. Veltmanplatz 8, D-52062 Aachen, Germany

Received 6 February 1998; accepted 6 May 1998

Abstract

The compressional relaxation performance of poly(tetrafluoro ethylene) (PTFE) in the α-transition region has previously been analysed and systematized using a two-component (TC) model. To further validate the consistency of the model and of the properties of its parameters, tanδ is calculated for extended ranges of temperature (from -50 to 250°C) and frequency (from 10^{-6} to 10^{8} Hz) and compared to dynamic mechanical as well as dielectric data. Modifying the original temperature dependence of one of the parameters of the model, namely of the characteristic relaxation time, leads to good qualitative and quantitative agreement between experiments and predictions for the whole experimentally accessed frequency (≈ 1 to 10^{7} Hz) and temperature range (120–200°C) of the α-transition. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Poly (tetrafluoro ethylene); α-transition; Dynamic performance

1. Introduction

To investigate the principles of time/temperature superposition for semicrystalline polymers, a two-component (TC) model was recently applied [1] to data of Araki [2] for the compressional relaxation performance of poly (tetrafluoro ethylene) (PTFE) in the α-transition region. The TC model relates to the empirical view that a semicrystalline polymer is a mixture of regions of different degrees of order ranging from crystallites to completely amorphous regions. As a limiting case the polymer is considered as a two-phase system [3] for which the principles of simple time/temperature superposition may not be applied [4–6]. The changes of the parameters of the TC model, based on fits of experimental data in the temperature range 60–140°C, reveal in the range of the α-process three individual transitions that have morphologically been attributed to the crystalline and the restricted amorphous phase [1], respectively.

The applicability of the TC model approach is supported by the good agreement between calculated tanδ results and data from torsional and bending experiments [1,7,8]. Furthermore, good general agreement is shown with other characteristic temperatures and transition phenomena in PTFE [1]

The various viscoelastic transitions in PTFE are well documented, e.g. Ref. [9]. Specifically, the transition temperatures of the α-process, given by the frequency dependent positions of the related tanδ peak, were compiled by McCrum et al. [9] for a wide range of frequencies. These data, originating from dynamic mechanical (●) as well as from dielectric tests (■), are presented in Fig. 1 for measuring frequency as log ν versus peak temperature T_p. The data are supplemented in the high frequency range by a result of Eby and Sinnott [10], applying ultrasonic analysis (+). The coherence of the results from dielectric and mechanical tests is interesting to note [9,11].

The objective of this paper is to take, on the basis of Ref. [1], a further step towards a consistent description of the viscoelastic performance of PTFE in the region of the α-transition. This is undertaken by investigating the applicability and plausibility of the specific principles of time/temperature superposition inherent to the TC model approach. The dynamic mechanical properties in the α-transition range of PTFE, namely tanδ, are calculated for wide ranges of temperature (-50 to $+250$) and frequency (10^{-6} to 10^{8} Hz), that are well outside the experimental window of Araki's creep tests. The frequency dependent tanδ peak positions on the temperature scale are determined and brought to agreement with the literature data. The typical and complex changes of the position, shape, and intensity of the tanδ peak with measuring frequency are evaluated and discussed.

1.1. Theory

The basis for the investigation are data on the compressional relaxation behaviour of PTFE sheet material (59% crystallinity), given by Araki [2] for a static time range of

PII: S0032-3861(98)00352-8

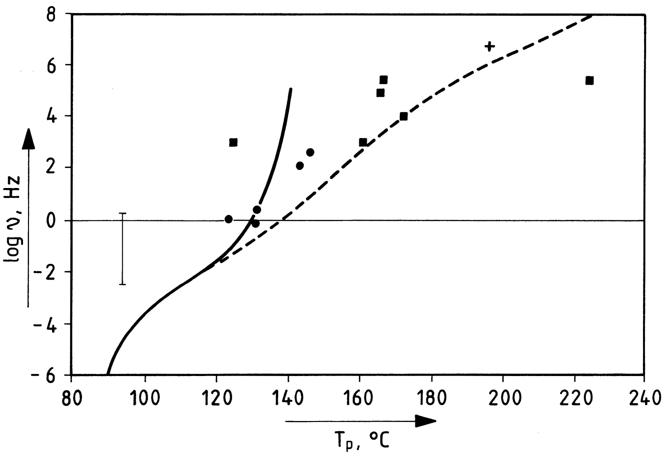

Fig. 1. Experimentally determined changes of the temperature position of the tanδ peak maximum T_p with frequency ν plotted as log ν versus T_p for the α-transition in PTFE. The data points originate from dynamic, mechanical (●, +) and dielectric tests (■) as given in Refs. [9,10]. The solid line gives peak position results, calculated on the basis of the initial results for the temperature dependence of the variables of the TC model. The broken line describes them on the basis of the revised estimate for the transition temperature of the characteristic relaxation time τ_c. The vertical bar marks the experimental window of the relaxation experiments (see text).

approx. 3–2000 s. To analyse the curves a TC model was applied [1], including time as well as temperature dependent effects:

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

E(t,T) is the time and temperature dependent, tensile relaxation modulus. E_∞(T) and $\Delta E(T)$ are the temperature dependent, elastic moduli of an elastic and a viscous component, so that ($\Delta E + E_\infty$) and E_∞ are the limiting moduli at short and at long times, respectively. $\Psi(t)$ is the relaxation function. From a morphological point of view and in the same way as for polypropylene [12], E_∞ and ΔE are attributed to the elastic response of the crystalline and of the rigid amorphous phase in PTFE, respectively [1].

Ψ(log t) is described here by using the cumulative log–normal distribution (CLND) function [1,13] given for the log(time) scale by:

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

τ_c is the characteristic relaxation time, $\log\tau_c$ the mean, and z the standard deviation of the underlying log–normal distribution. x is the integration variable on the log(time)-scale. As required by Kubat's experimental results [14,15], Φ(log t) forms a strictly symmetrical, sigmoid curve which drops from unity to zero within a range of approx. $\log\tau_c \pm 4z$. The material, strain and temperature invariance of the shape of the relaxation function, described by $z = 1.95$, has been shown for a variety of natural and synthetic polymers [1,12–16] .

The application of the TC model to Araki's [1,2] experimental results led to values for E_∞, ΔE and $\log\tau_c$ in Eqs. (1) and (2) for temperatures between 60 and 140°C, which in Arrhenius plots are empirically well described by sigmoid curves [1,12]:

$$y = a + \frac{b}{1+\exp[-(x-c)/d])} \tag{3}$$

where y is the logarithm of the parameter under consideration and $x = 1/T \times 10^3$ K. The constants a and b give the lower level and the intensity of the process, respectively; c gives the turnover point of the curve and d describes its width. The values for the constants, discussed in detail in Ref. [1], are given in Table 1. The curves described by them are given as solid lines in Fig. 2A and B for the linear temperature scale together with the data points they are based on. From the curves the transition temperatures T_{tr}, which are the turnover points of the curves given by the value of c, are obtained. They are marked on the curves in Fig. 2A and B as (o) and are summarized in Table 1.

Table 1

Values for the constants of the sigmoid fits (Eq. (3)) to the parameters of the TC model in Fig. 2 and the related transition temperatures T_{tr}, respectively

Sigmoid fit	E_∞	ΔE	τ_c (initial)	τ_c (revised)
a	7.53	5.69	0.20	− 4.10
b	2.82	2.44	2.23	6.60
c	3.37	2.29	2.54	2.35[a]
d	0.46	0.13	0.056	0.113
T_{tr}	24	163	120	152

[a] value introduced as restriction prior to curve fitting (see text)

The transition temperature for E_∞ (24°C) agrees well with the range for the first-order transition in the crystalline phase in PTFE between 19 and 30°C. The overall change is consistent with the gradual degradation of crystalline structure with temperature [17,18]. The transition temperatures for ΔE (163°C) and τ_c (initial fit: 120°C) fall into the range of the α-transition, as seen for example in dynamic mechanic experiments, between approx. 70 and 170°C and with a tanδ peak at $\approx$ 125–130°C [1,7,8]. The transition ranges are marked above the x axis of Fig. 2B.

Taking the theoretical parameter values from the sigmoid curves and applying Eqs. (1) and (2), tanδ is calculated for a given radial frequency ω according to [1,19]:

$$\tan\delta(\omega) = -\pi/2\,\frac{\mathrm{d}\log E}{\mathrm{d}\log t}\bigg|_{t=\frac{1}{\omega}} \tag{4}$$

yielding with Eq. (1) and including temperature effects:

$$\tan\delta(\omega,T) = -\ln 10\pi/2\,\frac{\Delta \mathrm{E}(T)\phi(t,T)}{\mathrm{E}_\infty(T)+\Delta \mathrm{E}(T)\Psi(t,T)}\bigg|_{t=\frac{1}{\omega}} \tag{5}$$

where $\Phi(t)$ is the first derivative of the relaxation function (Φt), namely the negative, underlying log–normal distribution.

The calculations were performed for the temperature range $-$ 50 to $+$ 250°C and for frequencies ν between 10^{-6} and 10^{8} Hz. For these Eq. (4) will give good estimates for the frequency-dependent location of the tanδ peak, while the estimates for peak height are expected to be of limited accuracy [3].

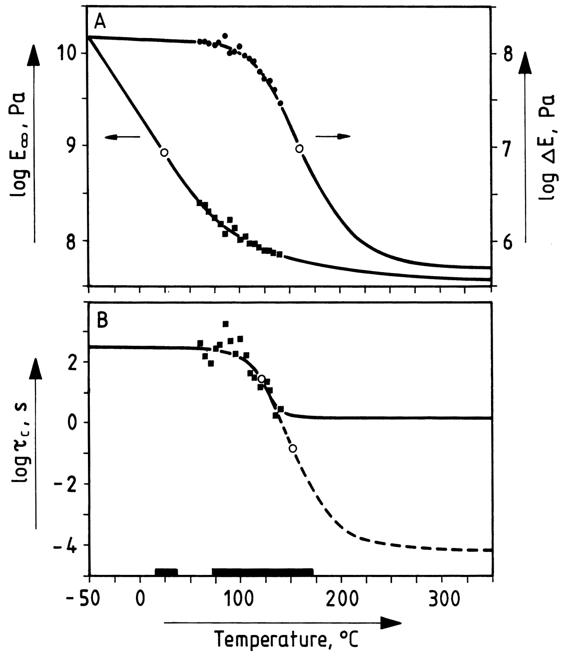

Fig. 2. (A) Experimental data for E_∞ and ΔE versus temperature and their descriptions, applying Eq. (3) and the constants in Table 1. (B) Experimental data for τ_c and the theoretical curves applying the 'initial' (———) and the 'revised' (- - -) constants. The specific transition temperatures are marked by (○). The bars above the x axis indicate the various transition ranges (see text).

The structure of Eq. (5) shows that, in the usual plot of tanδ versus temperature at a given frequency the properties of the tanδ peak are only partly controlled by the relaxation function and its first derivative. Strong further influences namely on intensity and shape are exerted by the relative magnitudes of the moduli and their individual temperature dependencies [1]. These will be specific for each semicrystalline polymer and are the source for the experimentally observed, pronounced changes of intensity and shape of their non-isothermal tanδ peaks, that are in a complex manner frequency related, e.g. Ref. [20].

1.2. Results and discussion

With the parameter values for Eq. (3) in Table 1 (listed as "initial" for τ_c), tanδ values for various frequencies were calculated on the basis of Eqs. (1), (2) and (5) in a spreadsheet application (QuattroPro, Novell). From the results the location of the tanδ peak on the temperature scale T_p was determined for various frequencies, yielding the solid line in Fig. 1. The vertical bar marks the frequency range, given by $\nu = \frac{1}{2\pi t}$, that reflects the experimental window of the static relaxation experiments.

The data points for dynamic mechanical and dielectric measurements taken from Refs. [9,10] are summarized in Fig. 1. They form an oblong data cloud that may well be described by a more or less straight or slightly curved line [9]. The solid line links up with the data range between 120 and 130°C. Above this temperature range it follows, however, a pronounced upward slope, showing in contradiction to the experimental results an unrealistic, asymptotic behaviour when approaching $T_\mathrm{p} \approx$ 140–145°C.

This lack of agreement with the experimental results starts in a temperature range (120–130°C) that coincides with the initial estimate from Ref. [1] for the transition temperature of log τ_c (120°C, see Table 1). This was taken as an indication that the transition temperature of the characteristic relaxation time was in fact underestimated by the initial set of parameter values for Eq. (3).

By introducing the value for c in Eq. (3) and thus the transition temperature of log τ_c as a restriction when fitting the equation to the experimental data, new fits to the data were generated after systematic and small incremental changes of c. Subsequently the log ν versus T_p relationship for each of the fits was determined. The broken line in Fig. 1, based on $c = 2.35$ for log τ_c, was graphically identified as the best fit to the experimental data, leading to $T_\mathrm{tr} = 152$°C (see Table 1) as a revised estimate for the transition temperature of log τ_c. The line, in fact, largely coincides with the empirical line drawn through the data by McCrum et al. [9] and documents the good coincidence of theory and experiments for the whole temperature (120–200°C) and frequency range (1–10^7 Hz) for which dynamic mechanical and dielectric results are available.

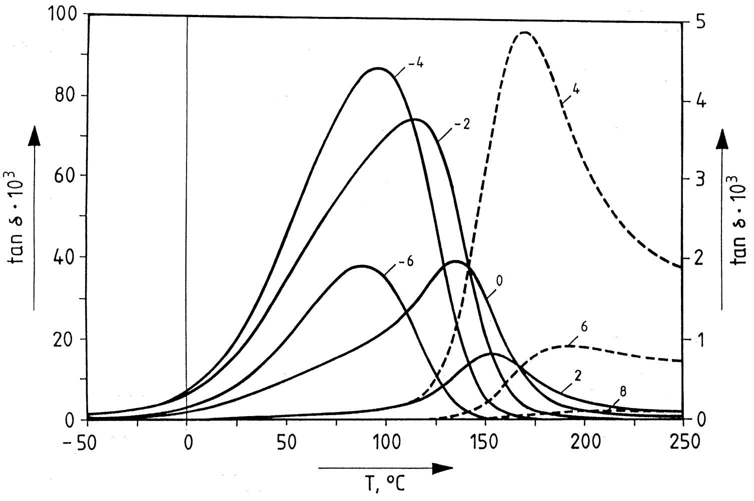

Fig. 3. Theoretical, non-isothermal tanδ curves for the frequency range 10^{-6} to 10^{8} Hz. The number attached to each curve gives log ν. (———) lines relate to the left and (- - -) lines to the right y axis.

The revised sigmoid fit for log τ_c is shown as a broken line in Fig. 2B. It has basically the same shape as the initial fit in the data range and the curves coincide on their upper levels. The lower limit is decreased by 4.3 decades, giving a significantly higher relaxation rate at higher temperatures compared to the initial description. The validity of the revision can be further substantiated by calculating the viscosity of the amorphous component of the TC model in the high-temperature range.

The viscosity of the viscous component is calculated according to Ref. [21]:

$$\eta = \Delta E \ 10^{z^2/2 + \log\tau_c} \ t* \quad (t* = 1 \text{ s}) \tag{6}$$

and on the basis of the curve for ΔE and with the revised values for τ_c in Fig. 2A and B, respectively.

This yields for low temperatures ($\approx$ $<$ 90°C) a value of 2.5×10^{14} Pa s. In view of the threshold viscosity of 10^{14} Pa s, that is generally applied to distinguish between solids and fluids, the value characterizes a soft and ductile, but still solid material, bordering in its properties on a highly viscous fluid. At 275°C the predicted viscosity has dropped by approximately nine decades to 3.3×10^{5} Pa s. This revised value [22] agrees well with the experimental value of 4.3×10^{5} Pa s determined by Starkweather [17] for the apparent viscosity of PTFE at that temperature, applying the DeWaele/Ostwald equation. A similar value can be derived from the investigation by McGee and Collier [23]. The values and the drop of the viscosity with temperature in the α-transition range are characteristic for a soft solid/fluid transition [22].

To further investigate the implications of the parameter fits shown in Fig. 2 theoretical results for tanδ for a wide range of frequencies were calculated and these predictions are summarized in Fig. 3. The frequencies were selected for the graph such as to show the shift of the peaks as well as their changes in height and skewness. Two y-scales, differing by a factor of 20, are chosen to accommodate the large changes in peak intensity over the whole frequency and temperature range. For low frequencies (10^{-6} to 10^{0} Hz) the peaks show a pronounced skewness towards the low temperature side. For higher frequencies (10^{2} Hz) they show symmetry to finally develop a pronounced skewness ($> 10^{4}$ Hz) towards the high temperature side. The results are in good qualitative agreement with those of Krum and Müller for dielectric spectroscopy [20]. All of these effects, namely the changes of tanδ peak shape and intensity, are rather typical for PTFE [7,24] and for semicrystalline polymers in general [9,25].

The investigation thus reveals a rather complex pattern of frequency dependent changes of the form, intensity and position of the tanδ peak on the temperature scale. They reflect the differences in the transition performance of the three parameters of the TC model and thus of the crystalline and rigid amorphous phase in PTFE, which control the dynamic mechanical performance in the α-transition region [1].

1.3. Conclusion

After revision of the specific temperature dependence of one of the parameters of the TC model, namely of the characteristic relaxation time, consistency is achieved with dynamic mechanical and dielectric, as well as viscosity data over wide ranges of temperature and frequency. This identifies the model as a physically robust approach for the quantitative analysis of the temperature dependence of the viscoelastic performance of PTFE and possibly for semicrystalline polymers in general in their α-transition region.

References

[1] Wortmann F-J. Polymer 1996;37:2471.
[2] Araki Y. J Appl Polym Sci 1965;9:1515.
[3] Schwarzl FR. Polymer Mechanik. Berlin: Springer Verlag, 1990.

[4] Nagamatsu K. Kolloid Z 1960;172:141.
[5] Wortmann F-J, Schulz KV. Polymer 1995;36:1611.
[6] Tobolsky AV, McLoughlin JR. J Phys Chem 1955;59:989.
[7] Khanna YP, Chomyn G, Kumar R, Murthy NS, OBrien KP, Reimschuessel AC. Macromolecules 1990;23:2488.
[8] McCrum NG. J Polym Sci 1959;34:355.
[9] McCrum NG, Read BE, Williams G. Anelastic and dielectric effects in polymeric solids. London: Wiley, 1967.
[10] Eby RK, Sinnott KM. J Appl Phys 1961;32:1765.
[11] Wada Y. J Phys Soc Jap 1961;16:1226.
[12] Wortmann F-J, Schulz KV. Polymer 1996;37:819.
[13] Wortmann F-J, Schulz KV. Polymer 1995;36:315.
[14] Kubat J. Nature 1965;205:378.
[15] Wortmann F-J, Schulz KV. Polymer 1994;35:2108.
[16] Wortmann F-J, DeJong S. Text Res J 1985;55:750.
[17] Starkweather HW Jr. J Polym Sci Polym Phys Edn 1979;17:73.
[18] Macturk KS, Farmer BL, Eby RK. Polymer Int 1995;37:157.
[19] Struik LCE. Polymer 1987;28:1521.
[20] Krum F, Müller FH. Kolloid Z 1959;164:82.
[21] Wortmann F-J, Schulz KV. Polymer 1995;36:2363.
[22] Wortmann F-J. In: Merchant HD, editor. Creep and stress relaxation in miniature structures and composites. Warrendale: The Mineral, Metals, Materials Society, 1997:105.
[23] McGee RL, Collier JR. Polym Eng Sci 1986;26:239.
[24] McCrum NG. J Polym Sci 1958;27:555.
[25] Goodwin AA, Simon GP. Macromolecules 1995;28:7022.