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Investigations on the thermorheological simplicity of polypropylene fibres in the α-transition range

F.-J. Wortmann* and K. V. Schulz
Deutsches Wollforschungsinstitut, Veltmanplatz 8, D-52062 Aachen, Germany
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In a recent publication the authors reported investigations on the relaxation behaviour of isotactic polypropylene fibres in the α-transition range. The results of the analysis of relaxation curves on the basis of a two-component model were incompatible with those of a previous investigation by Faucher, who found thermorheological simplicity (TRS) for the material. This paper investigates this incompatibility, by checking whether the relaxation curves previously obtained can alternatively be systemized on the basis of the TRS principle. It is shown that the curves superimpose to yield a satisfactory master curve. However, calculating dynamic mechanical properties, i.e. $\tan\delta$, from this master curve leads to a pronounced inconsistency with experimental results. Thus it may be concluded that the TRS principle is only an empirically successful data reduction method that does not adequately model the time–temperature superposition for semicrystalline polypropylene and is hence not applicable for a reliable prediction of its long-term viscoelastic performance.

(Keywords: viscoelasticity; thermorheology; time–temperature superposition; isotactic polypropylene fibres)

INTRODUCTION

In a recent publication[1] 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 ($\varepsilon < 2\%$), relating to the α-transition of the polymer.

Following the usual approach[2], the relaxation curves were analysed by applying a two-component (TC) model:

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

where $E_\infty(T)$ and $\Delta E(T)$ are the temperature-dependent, limiting elastic moduli of an elastic and a viscoelastic component, respectively. $\Psi(t)$ is the relaxation function, described in ref. 1 on the basis of the cumulative log normal distribution. It forms a strictly symmetrical, S-shaped curve on the log(time) scale, the shape of which is independent of temperature. a_T is the acceleration factor, or as $\log(a_T)$ referred to as the shift factor, describing the displacement of the relaxation function on the log(time) scale to shorter times with increasing temperature.

The application of the TC model reveals the pronounced influence of temperature on the moduli and only moderate changes of the shift factor, all of which may be described by Arrhenius relationships with activation energies between 10 and 30 kJ mol^{-1} above the transition temperature around −15°C. In these properties the results of the model are incompatible with those of past investigations by Faucher[3] on isotactic polypropylene.

Faucher[3] found that his relaxation curves on a log(modulus) *versus* log(time) plot for temperatures between −67 and 140°C could be superposed by strictly horizontal shifts, this representing a so-called thermorheologically simple (TRS) material[4] described by:

$$E(T) = E_0\Phi(t/a_T) \qquad (2)$$

where E_0 is the temperature-independent upper limiting modulus and Φ is the relaxation function. This behaviour has classically been observed and analysed by Catsiff and Tobolsky[5] for polyisobutylene.

The apparent success of the TRS principle was also observed for amorphous polypropylene by Plazek and Plazek[6]. However, the differences in the temperature dependences of viscosity and compliance measurements led them to conclude that the TRS principle could not be a valid description of the time–temperature superposition performance.

This investigation is concerned with two questions: (1) whether stress relaxation curves for isotactic, semicrystalline polypropylene fibres, analysed in ref. 1 on the basis of equation (1), can alternatively and much more simply be described by the TRS principle (equation (2)) and (2) whether the results of such an analysis are consistent with the dynamic mechanical performance of the material.

MATERIALS, METHODS, PRINCIPLES OF DATA ANALYSIS AND RESULTS

All data come from single-step stress relaxation experiments for isotactic polypropylene fibres (Vestolen P2000 CR, Chemische Werke Hüls AG), as described in ref. 1.

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* To whom correspondence should be addressed

The experiments were conducted on an Instron (type 1122) tensile tester in a temperature range of −50 to 30°C, for strains up to 2% and for times of up to 8000 s. The extensional, dynamic mechanical test (see *Figure 5*) was performed on a Gabo Qualimeter (Fa. Gabo, Ahlden/Aller) at 2 Hz and a static strain of 1% with a superimposed dynamic strain of ±0.4% in the temperature range of −100 to +100°C.

Figure 1 summarizes a representative set of curves of log(modulus) *versus* log(time) of the investigated temperature range. Taking the curve for 30°C as reference, a master curve was constructed by horizontally shifting the other curves to shorter times until, from a subjective point of view, a good superposition was achieved. As shown in *Figure 2*, these master curve data are well described ($r^2 > 0.999$) by a fourth-order polynomial as:

$$\log(E) = a + bx + cx^2 + dx^3 + ex^4 \qquad (3)$$

with

$$x = \log(t/a_T) \qquad (4)$$

the parameters for which (a–e) are given on the graph together with the polynomial line.

The fact that curves at similar temperatures may describe quite different parts of the master curve (see curves for −42 and −47°C in *Figure 2*) reflects the fact

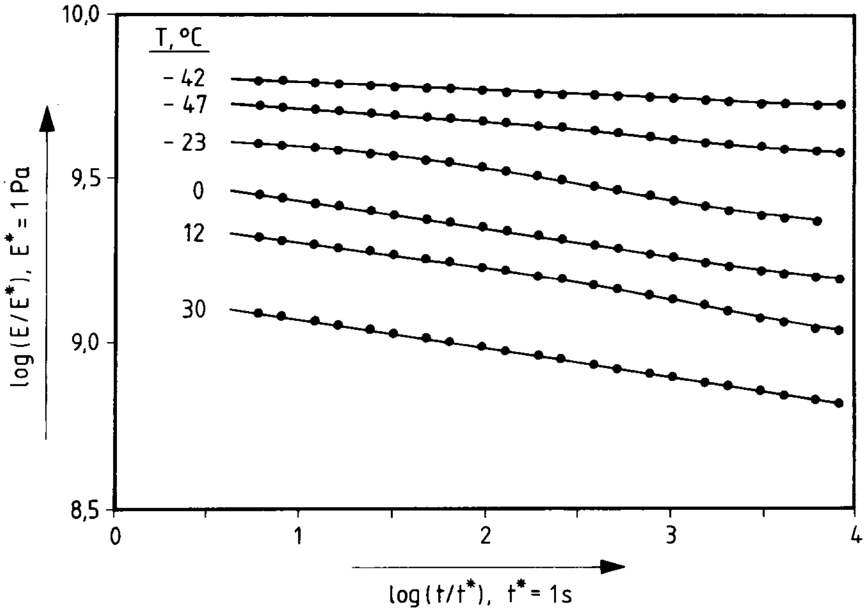

Figure 1 Representative set of log(relaxation modulus) *versus* log(time) curves for the investigated temperature range. The solid lines through the data serve purely descriptive purposes

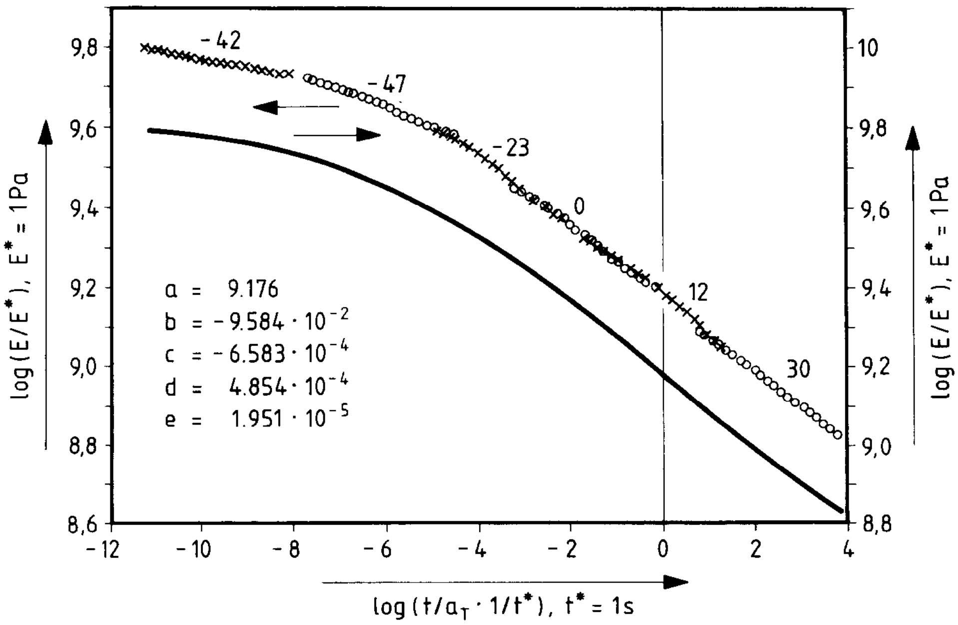

Figure 2 Master curve generated by superposition of the curves in *Figure 1* (upper curve) and its description by a fourth-order polynomial (lower curve) of which the parameters are given. The curves are vertically offset for reasons of clarity. The figures along the upper curve give the temperatures for the curve fragments. Reference temperature is 30°C

that, for an individual curve, any experimental error in the determination of strain or cross-sectional area will in reality lead to a vertical offset of the curves. This, however, has to be compensated for within the framework of the TRS principle by horizontal shifts which, due to the small curvature of the relaxation curves at low temperature, may be rather substantial.

The polynomial was taken as the definitive description of the TRS master curve onto which all 43 experimental curves were fitted using the least-squares criterion for the log(modulus) data by applying the non-linear optimization routine implemented in QUATTRO PRO (Borland). The modulus curve in *Figure 3* shows how the experimental data cluster onto the master curve. For reasons of clarity, only about half the experimental curves were used for the plot.

Figure 4 summarizes the shift factors with respect to the specific reference curve at 30°C in an Arrhenius plot. The data follow a straight line well ($r^2 > 0.85$) giving an activation energy of $150 \pm 20\,\mathrm{kJ\,mol^{-1}}$, in reasonable agreement with Faucher's[3] results ($\Delta E = 210\,\mathrm{kJ\,mol^{-1}}$) and other literature data[7] (117–152 kJ mol^{-1}).

DISCUSSION

The success of the formation of the master curve in *Figures 2* and *3* shows that the simple horizontal superposition on the log(time) scale, that is the treatment of isotactic polypropylene fibres as a thermorheologically simple material, appears to be a successful principle. The results seem to confirm the general applicability of the TRS principle and its widespread use for the prediction

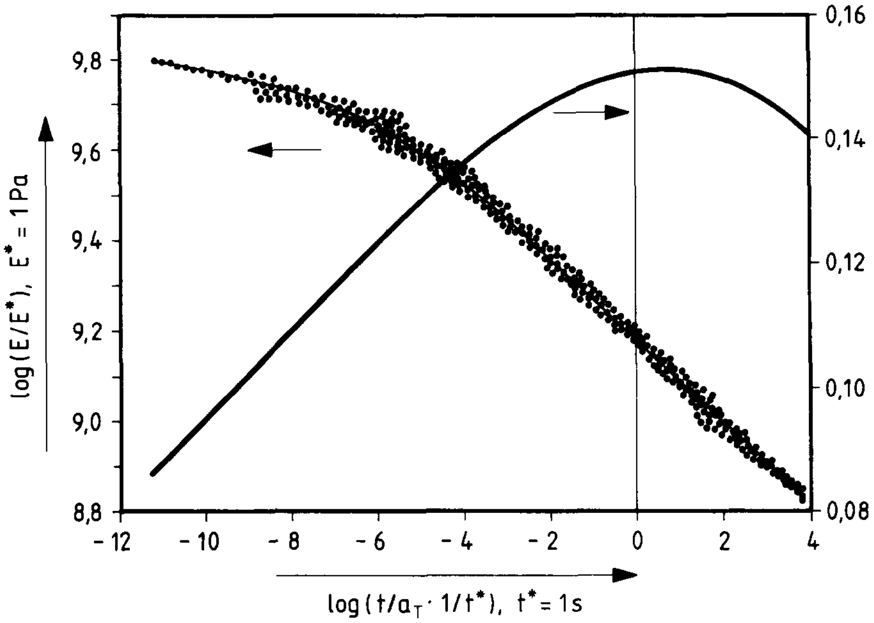

Figure 3 Superposition of individual experimental relaxation curve data onto the master curve by strictly horizontal shifts, and tan δ for the fitted master curve

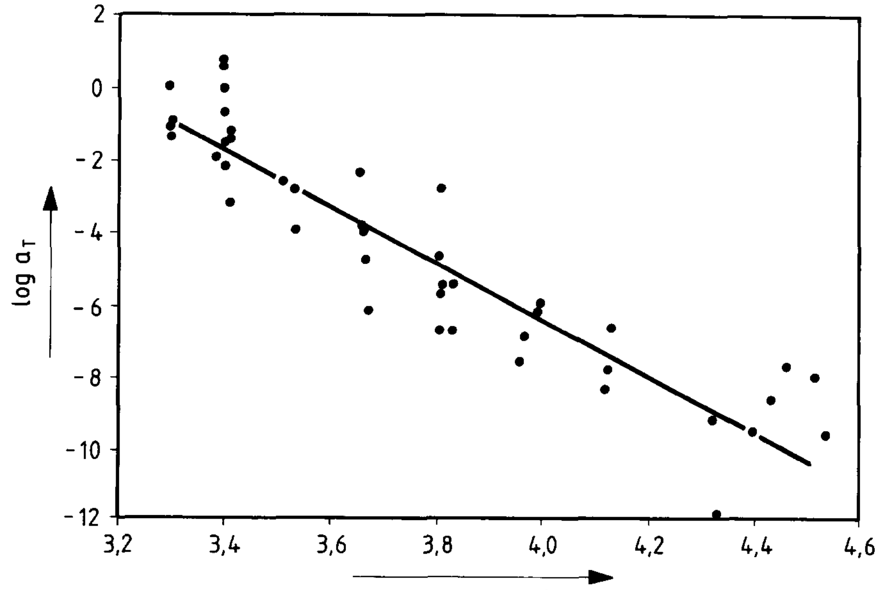

Figure 4 Shift factors for the individual experimental curves *versus* inverse temperature (Arrhenius plot) for a reference temperature of 30°C

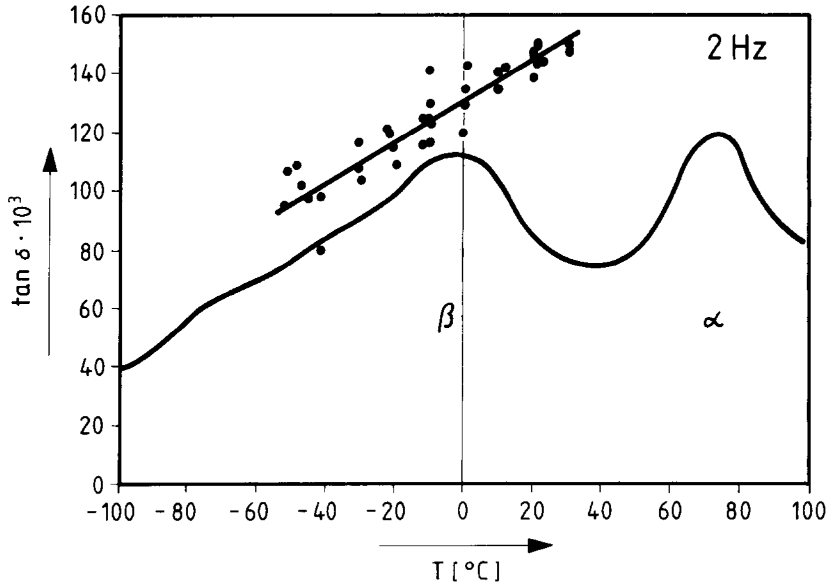

Figure 5 Tan δ results *versus* temperature from a dynamic mechanical experiment (——) at 2 Hz and values calculated from the individual static relaxation curves (●) via the master curve and applying equation (5) together with the shift factors in *Figure 4*. The relaxation transitions are indicated

of the long-term performance of a wide variety of polymers, whether they be elastomeric, thermoplastic, partially crystalline or filled (see, for example, ref. 8).

However, an obvious flaw of the physical plausibility of the description is the fact that neither the modulus, which is constant with temperature, nor the shift factor give any indication of the existence of the glass transition, to be expected[6,7] somewhere between −20 and −10°C. The shift factor in particular would be expected to show a discontinuity at the glass transition temperature, similar to that for amorphous polypropylene[3]. According to the Adam–Gibbs entropy model[9], the temperature dependence of the shift factor would be expected to change from an Arrhenius towards a Williams–Landel–Ferry (WLF)[10] type relationship.

To evaluate the validity of the application of the TRS principle, its consistency was checked (as was that of the TC model in ref. 1) against the results of a dynamic mechanical measurement, namely of tan δ.

Figure 5 summarizes the tan δ data for the material for the temperature range −100 to +100°C, revealing two well separated transitions with maxima at −5 and +70°C that are quite similar in shape and identified as the α- and β-transition, respectively[11]. The β-relaxation is usually assumed to relate to the bulk amorphous phase that is associated with the main glass transition, while the α-process involves motions of the restrained amorphous component in the vicinity of the crystals[12].

On the basis of the master curve description according to equation (3), tan δ was calculated as:

$$\tan\delta(\omega) = -(\pi/2) d\log E/d\log t|_{1/\omega=t} \qquad (5)$$

and is given for the time scale in *Figure 3*. Applying the individual shift factors of the experimental curves as given in *Figure 4*, the tan δ values for 2 Hz are calculated for the temperature scale and summarized in *Figure 5*.

The tan δ values derived from the TRS master curve follow in parallel the low temperature slope of the β-relaxation peak of the dynamic mechanical spectrum. The systematic difference between the two sets of curves in this range is ~0.02, which, in view of potential errors in the determination of the theoretical values, is considered as acceptable. However, the β-transition shows a tan δ peak around −5°C, which is not reproduced by the theoretical values.

Furthermore, the calculated tan δ data relate to the low temperature region of the β-transition. This is inconsistent with Read's[13,14] and our results[1] that quite conclusively show that the relaxation process described by the experimental curves is actually the α-process. Thus, the wrong dynamic mechanical relaxation process is modelled by the application of the TRS principle to the static relaxation data.

The results therefore show that for semicrystalline polypropylene the TRS principle is only an empirically successful data reduction system that does not adequately model the real time–temperature superposition of the material and is hence not applicable for a reliable prediction of its long-term viscoelastic performance. This consequence also applies to the validity of kinetic analysis methods of dynamic mechanical data that rely inherently on the thermorheological simplicity of the material.

Our conclusions are in agreement with the experimental observation of Maxwell and Heider[15] on the complexity of the thermorheological performance of the material. Furthermore, the problems with the applicability of the TRS principle for polypropylene are consistent with the observations reviewed by Schapery[16] and Boyd[11] who pointed out that generally horizontal as well as vertical shifts in a log(modulus) *versus* log(time) plot are necessary for semicrystalline polymers, making these materials thermorheologically complex (TRC).

The TRC principle introduces another parameter (vertical shift in a log(modulus) *versus* log(time) plot) that might possibly model the physical reality of the material more realistically. However, in view of the shape of the master curve in *Figure 2*, with little curvature for short times and an extended linear region for longer times, the decision for vertical rather than horizontal shifts would for most of the curves not be unambiguous, even if more elaborate methods for superposition were used[17].

Hence the TRC principle does not provide a feasible path towards a realistic superposition method.

The results favour the two-component model (equation (1)) rather than the traditional TRS principle to arrive at reliable predictions for the long-term viscoelastic performance of isotactic polypropylene and other semicrystalline polymers[18]. Current work is directed at an evaluation of Faucher's data[3] on the basis of the two-component model. The temperature range of Faucher's experiments well exceeds that of our own experiments, so that the data are especially suited to check further the consistency of this special form of a time–temperature superposition principle.

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