Colloid Polym Sci 275:116–123 (1997)

ORIGINAL CONTRIBUTION

S. Hellinckx

Mechanical behaviour of isotactic polypropylenes in the lower and the upper glass transitions ranges

1. Linear behaviour

Received: 2 January 1996
Accepted: 16 August 1996

Dr. S. Hellinckx (✉)
Solvay (LC604)
Rue de Ransbeek 310
1120 Brussels, Belgium

Abstract The effects of physical ageing on both glass transitions of isotactic polypropylenes (homopolymer and random copolymer) are investigated by isothermal dynamic mechanical spectroscopy and by low strain creep. The ageing-time dependent expressions of the amorphous fractions which undergo each relaxation are introduced in a rheological model composed by a modified Zener model (associated to the β-relaxation) in series with a γ-element (associated to the α-relaxation). The agreement between the responses of this model and the creep and dynamic results is good over a time (or frequency) range covering up to 15 decades for three kinds of isotactic polypropylenes.

Key words Isotatic polypropylenes – lower and upper glass transitions – low strain creep – dynamic mechanical spectroscopy – physical ageing

Introduction

It is now quite well accepted that semi-crystalline polymers exhibit two glass transitions [1]: a lower one (the β-relaxation) which is associated to molecular motions occurring in the bulk amorphous phase and an upper one (the α-relaxation) which results from coupled motions in the amorphous and in the semi-crystalline phases [1–5].

These transitions are considerably affected by physical ageing performed at temperatures located between both relaxation processes [6, 7]. In particular, in the case of polypropylene, physical ageing produces a decrease of the magnitude of the β-relaxation [8, 9] and an increase of the magnitude [10] and of the time constant [8–10] of the α-relaxation. In a previous paper, a model has been proposed that accounts for the variations of the fractions of amorphous material which undergo both relaxations [10]. This model, which considers deformation as a diffusion process [11], is in good agreement with experimental linear creep data obtained on isotactic polypropylenes at creep times longer than 1 s, i.e., at creep times located in the α-relaxation region.

The purpose of this paper is to propose a model able to describe the effect of physical ageing on dynamic mechanical data and on creep data in a time window covering the β and the α relaxations.

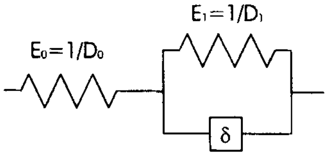
Model

Rheological model in the β-range

In isothermal dynamic measurements performed at room temperature at frequencies between 10^8 and 1 Hz, the β-relaxation gives rise to a loss peak [9] and can therefore be described by a Zener model whose dashpot is replaced by a δ-element [12] in order to stretch the relaxation over a wide frequency range (Fig. 1).

Heymans and Bauwens [12] proposed a viscoelastic element (called δ-element) whose response, in the

Fig. 1 Modified Zener model associated to the β-relaxation of iPP



frequency domain, is given by $D^* = D_b(i\omega\tau_\beta)^{-\delta}$ corresponding to a fractional differential time domain equation

$$\sigma = \frac{1}{D_b}\frac{d^{\delta}\varepsilon}{d\left(\frac{t}{\tau_\beta}\right)^{\delta}} \quad \text{or} \quad \varepsilon = D_b\frac{d^{-\delta}\sigma}{d\left(\frac{t}{\tau_\beta}\right)^{-\delta}}$$

where D_b and τ_β denote a compliance and a time constant respectively. The δ-exponent has a value between 0 and 1.

This element, introduced into a Zener model (Fig. 1), yields to the Cole–Cole behaviour

$$D^*_\beta(\omega) = D_0 + \frac{D_1}{1 + \frac{D_1}{D_b}(i\omega\tau_\beta)^{\delta}} \tag{1}$$

where D_0 and D_1 are compliances. This relation allows a broad relaxation to be described with a very small number of fitting parameters (typically 3 per transition).

The creep response $D_\beta(t)$ can be calculated numerically by two different ways. The first one, used by Heymans [13], consists in solving the differential equation of fractional order arising from the model. The second one which is based on the Boltzmann superposition principle requires only simple mathematical procedures.

Let us consider the Kelvin–Voigt model formed by the spring (whose modulus is $E_1 = 1/D_1$) in parallel with the δ-element. We can consider that the stress applied to this element is the sum of the stress it would undergo in the absence of the spring and of the compressive stress due to the fact that the spring progressively unloads the δ-element. At a creep time t, the compliance of the δ-element related to the unloading by the spring at a time t_i is

$$D(t - t_i) = \frac{D_b}{\Gamma(1+\delta)}\left(\frac{t - t_i}{\tau_\beta}\right)^{\delta} \tag{2}$$

where Γ is the gamma function. The compressive deformation $\varepsilon_c(t)$ resulting from all the unloadings $\Delta\sigma_V(t_i)$ can be calculated from the Boltzmann superposition principle

$$\varepsilon_c(t) = \frac{D_b}{\Gamma(1+\delta)}\sum_i \frac{\Delta\sigma_V(t_i)}{\Delta t_i}\left(\frac{t - t_i}{\tau_\beta}\right)^{\delta}\Delta t_i\,. \tag{3}$$

Since the applied stress σ is connected to the total instantaneous strain $\varepsilon(t_i)$ through $\sigma = \frac{\varepsilon(t_i)}{D_1} + \Delta\sigma_V(t_i)$, Eq. (3) can be rewritten as

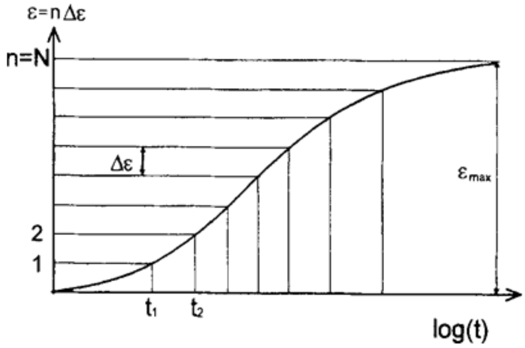


Fig. 2 Schematic representation of the mathematical procedure used in order to calculate the creep response of a modified Kelvin–Voigt element

$$\varepsilon_c(t) = -\frac{D_b}{D_1\Gamma(1+\delta)}\sum_{t_i=0}^{t_i=t}\Delta\varepsilon(t_i)\left(\frac{t - t_i}{\tau_\beta}\right)^{\delta}. \tag{4}$$

Therefore the total strain is

$$\varepsilon(t) = \frac{D_b\sigma}{\Gamma(1+\delta)}\left(\frac{t}{\tau_\beta}\right)^{\delta} + \varepsilon_c\,. \tag{5}$$

If $\varepsilon(t)$ is transformed into a sum of N intervals $\Delta\varepsilon$ (see Fig. 2), Eq. (5) becomes

$$n\Delta\varepsilon = \frac{D_b}{\Gamma(1+\delta)}\left[\sigma\left(\frac{t_n}{\tau_\beta}\right)^{\delta} - \frac{1}{D_1}\sum_{t_i=0}^{t_i=t_n}\Delta\varepsilon\left(\frac{t_n - t_i}{\tau_\beta}\right)^{\delta}\right] \tag{6}$$

where n is an integer. At very long times, the spring is submitted to the applied stress and

$$\varepsilon(t \to \infty) = \sigma D_1 = N\Delta\varepsilon\,. \tag{7}$$

Taking (7) into account, Eq. (6) can be rewritten as

$$n = \frac{D_b}{D_1\Gamma(1+\delta)}\left[N\left(\frac{t_n}{\tau_\beta}\right)^{\delta} - \sum_{t_i=0}^{t_i=t_n}\left(\frac{t_n - t_i}{\tau_\beta}\right)^{\delta}\right]. \tag{8}$$

This equation can be solved numerically: for each value of n between 1 and N, the corresponding time t_n is determined. The creep compliance can therefore be expressed by

$$D_\beta(t) = D_0 + \frac{n(t)}{N}D_1 \tag{9}$$

where D_0 represents the instantaneous creep compliance.

Rheological model in the α-range

The α-relaxation occurs at times larger than 10^{-2} s when the β-process is nearly completely relaxed [9]. The unrelaxed compliance of the α-process is then close to the

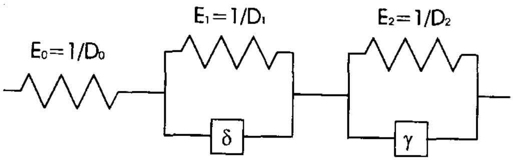


Fig. 3 Complete rheological model describing the mechanical behaviour of iPP through both glass transitions

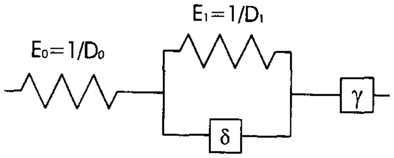


Fig. 4 Simplified rheological model describing the mechanical behaviour of iPP through both glass transitions

relaxed compliance of the β-process and the simplest model able to describe the behaviour in a time range covering both transitions consists therefore of a modified Zener model (associated with the β-process) in series with a modified Kelvin–Voigt model (associated with the α-process) (Fig. 3).

The dynamic response of such a model can be calculated from

$$D^*(\omega) = D^*_\beta(\omega) + D^*_\alpha(\omega) \tag{10}$$

where $D^*_\beta(\omega)$ is given by Eq. (1) and where

$$D^*_\alpha(\omega) = \frac{D_2}{1 + \dfrac{D_2}{D_a}(i\omega\tau_\alpha)^\gamma} \tag{11}$$

D_2 and D_a are compliances and τ_α denotes a time constant.

The creep response $D(t)$ is the sum of the creep compliances $D_\beta(t)$ and $D_\alpha(t)$ related to both glass transistions. $D_\beta(t)$ can be determined numerically from equations (8) and (9) and $D_\alpha(t)$ by solving Eq. (8) where D_1, D_b, τ_β and δ must be replaced by D_2, D_a, τ_α and γ respectively.

The calculation of $D(t)$ becomes simpler in the particular case where the maximum creep time is much shorter than the time constant of the Kelvin–Voigt model associated to the α-process. The creep response of this model is then closely approximated by to the response of the γ-element

$$D_\alpha(t) = \frac{D_a}{\Gamma(1+\gamma)}\left(\frac{t}{\tau_\alpha}\right)^\gamma . \tag{12}$$

It is interesting to note that this expression is similar to the one obtained by considering that deformation results from a diffusion process [10].

In the following sections of this paper, we will opt for the simplified model arising from this particular case (Fig. 4). A great advantage of this simplification is to eliminate the parameter $E_2 (E_2 = 1/D_2 = 0)$ whose accurate evaluation requires either creep data at times much longer than τ_α or isothermal dynamic data at frequencies corresponding to the low frequency side of the α-peak. Since none of these data are available in the case of iPP, the choice of the simplified model appears very appropriate.

Effect of physical ageing

It is well known that the molecular motions associated to the β-relaxation (the lower glass transition), located around 275 K, occur in the amorphous phase of polypropylene. Moreover, as mentioned previously [10], the α-relaxation process (the upper glass transition) induces motions of non-crystalline chain segments having a helical conformation. It was also shown [10] that physical ageing affects on one hand the fractions of amorphous material which undergo each glass transition and, on the other hand the time constant of the α-relaxation.

Considering that the $\beta \rightarrow \alpha$ transformation is a diffusion process, we have found [10] that the expressions of the amorphous fractions are

$$\alpha = A t_a^\varphi \tag{13}$$

$$\beta = 1 - A t_a^\varphi \tag{14}$$

where t_a denotes the ageing time, A is a constant and φ a parameter between 0 and 1.

As shown previously [10, 14], the expression of the time constant of the α-process is

$$\tau_\alpha = \tau_0 \left(\frac{t_a}{\tau_0}\right)^\mu \tag{15}$$

in the case of dynamic or short term creep tests and

$$\tau_\alpha = \tau_0 \left(\frac{t + t_a}{\tau_0}\right)^\mu \tag{16}$$

in the case of long term creep tests. In Eqs. (15) and (16), τ_0 denotes a constant and μ is the Struik's parameter whose value is close to 1.

Equation (16) must be introduced in the differential expressions of the creep compliance $D_\alpha(t)$: either the classical differential equation resulting from a diffusion model, or the differential equation of fractionnal order. The former has been solved previously [10] and gives rise to

$$D_\alpha(t) = \frac{D_a}{\Gamma(1+\gamma)}\left(\frac{1}{\tau_0^{1-\mu}(1-\mu)}\right)^\gamma [(t_a + t)^{1-\mu} - t_a^{1-\mu}]^\gamma \quad \text{if } \mu \neq 1 \tag{17}$$

$$D_\alpha(t) = \frac{D_a}{\Gamma(1+\gamma)}\left[\ln\left(1+\frac{t}{t_a}\right)\right]^\gamma \quad \text{if } \mu = 1 \, . \tag{18}$$

The latter can be rewritten, by taking (16) into account, as

$$D_\alpha(t) = \frac{1}{\sigma}\frac{D_a}{\tau_0^{\gamma(1-\mu)}}\frac{d^{-\gamma}}{dt^{-\gamma}}\left(\frac{\sigma}{(t_a+t)^{\gamma\mu}}\right) . \tag{19}$$

The numerical solution of Eq. (19) is compared to Eq. (17) on Fig. 5. The values of the parameters are $D_a = 1\ \text{GPa}^{-1}$, $\tau_0 = 1$ s, $\gamma = 0.25$ and $\mu = 0.8$ and the ageing time is $t_a = 1$ s in both cases. It can be seen that both curves superpose at creep times shorter than t_a. On the contrary, at times longer than the ageing time, this equivalence is no longer valid; the compliance calculated from the diffusion process becomes greater than the compliance resulting from the fractional differential equation. For simplicity, we will choose the former when comparing theoretical curves with experimental results.

Response of the rheological model in presence of physical ageing

In order to describe the mechanical behaviour of samples of iPP of different ages, relations (13) and (14) must be introduced in the dynamic and in the creep responses of the model of Fig. 4. In this model, the Kelvin–Voigt and the γ-elements are associated to the lower and to the upper glass transitions respectively. Since their respective maximum compliance is limited by the amount of amorphous material undergoing each of them, the expression of

a) the complex compliance is

$$D^*(\omega) = D_0 + \beta(D_\beta^*(\omega) - D_0) + \alpha D_\alpha^*(\omega) \tag{20}$$

where α and β are given by Eqs. (13) and (14) respectively and $D_\beta^*(\omega)$ and $D_\alpha^*(\omega)$ by Eqs. (1) and (11) (taking $E_2 = 1/D_2 = 0$) respectively. The value of τ_α appearing in Eq. (11) can be obtained from relation (16).

b) The creep compliance is

$$D(t) = D_0 + \beta(D_\beta(t) - D_0) + \alpha D_\alpha(t) \tag{21}$$

where α, β and $D_\beta(t)$ are given by Eqs. (13), (14) and by combinating Eqs. (8) and (9) respectively. With regards to $D_\alpha(t)$, this compliance can be expressed

- at short times: by Eq. (12) taking (15) into account
- at long times: by Eq. (17) or Eq. (18).

Experimental

Material

A commercially-available isotactic polypropylene is used. This iPP is a random copolymer (2–3% ethylene) supplied by Solvay under the trade name Eltex P KS409. It is characterized by a quite low crystallinity (around 35%) and has a MFI between 5 and 8 g/10 min (ASTM D1238).

The tensile creep and the dynamic specimens were machined from extruded sheets of 1.2 or 2 mm thick.

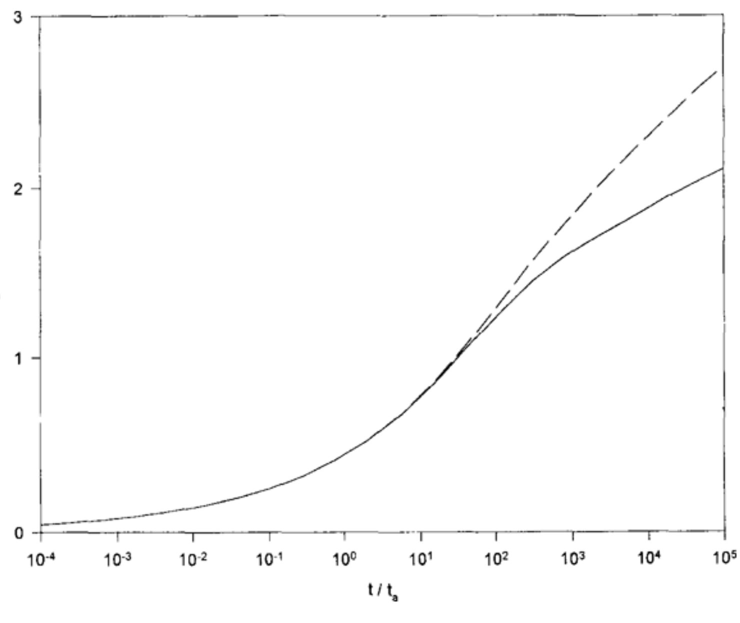


Fig. 5 Comparison of theoretical long-term creep curves calculated from the differential equation associated to a diffusion model (dashed line) and from the differential equation of fractional order resulting from a γ-element (full line)

Thermal treatments

In order to erase previous effects of ageing, all the samples are annealed at 100 °C for 4 h [10]. After quenching in water at room temperature, the samples are aged at 30 °C in an environmental chamber.

Creep tests

Tensile low strain creep tests are performed at 30 °C on dumbbell-shaped specimens with a gauge length of 40 mm and a cross-section of 8×2 mm^2. The apparatus has been described previously [10].

Dynamic mechanical tests

Two techniques are used: ultrasonics at frequencies between 0.2 and 6 MHz and tensile resonance in the audio-frequency range (0.1 to 2 kHz). These techniques have been widely described by Read et al. [15, 16]. In both cases, the tests are performed at 30 °C.

Comparison of the model with the data

The response of the proposed model is compared, on one hand, with results we obtained on a random PP copolymer and, on the other hand, with data from the literature related to PP homopolymers.

Isothermal dynamic measurements

The loss compliance from Eq. (20) is compared in Fig. 6 with Read et al.'s results [9] obtained on iPP homopolymer (Propathene from ICI) stored at 23 °C for ageing times of 2.5 and 216 h prior to the mechanical test. The values of the parameters are reported in Table 1. The agreement of the model is rather good in the whole frequency window covering the β-process and the high frequency side of the α-process. It is interesting to note that the use (made by Heymans [13]) of a nested model instead of a series model improves the fit in the frequency range covering the high frequency tail of the α-relaxation.

The storage Young modulus obtained at 30 °C on iPP random copolymer (aged between 2 and 200 h) is plotted versus frequency in Fig. 7. Since the investigated frequency range covers mostly the β-relaxation, the contribution of the α-relaxation is negligible and the theoretical equation used is

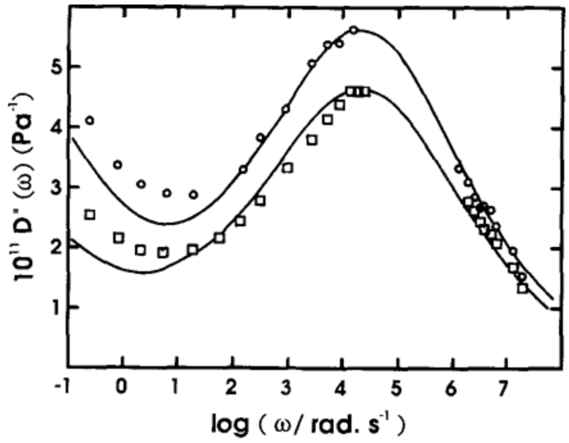


Fig. 6 Loss compliance obtained by Read et al. [9] on Propathene (ICI) stored ○ 2.5 and □ 216 h at 23 °C. The full curves are calculated from Eqs. (1), (11), (13)–(15) and (20) by taking $E_2 = 1/D_2 = 0$. The parameters are given in Table 1

Table 1 Parameters for Propathene from ICI

Parameter	Value	Unit
D_0	0.210	GPa^{-1}
D_1	0.667	GPa^{-1}
D_b/τ_β^δ	21	GPa^{-1} s$^{-0.345}$
δ	0.345	–
A'	0.241	s$^{-0.0525}$
φ	0.0525	–
$D_a/\tau_0^{\gamma(1-\mu)}$	0.837	GPa^{-1} s$^{-0.0525}$
γ	0.25	–
μ	0.79	–

$$E'(\omega) = \Re e\left[\frac{1}{D_0 + \beta(D_\beta^*(\omega) - D_0)}\right] \qquad (22)$$

where $\Re e$ indicates that the real part is considered. The parameters giving the best fit are given in the upper part of Table 2.

Short term creep tests

In Fig. 8, the response of the model (Eqs. (12), (15) and (21)) is compared with creep data related to iPP homopolymer (Propathene from ICI) aged 2.5 and 216 h at 23 °C [9]. The data corresponding to times lower than a second have been obtained from dynamic measurements by using the Hamon approximation [17]. The data corresponding to longer times are true creep data. The theoretical curves are calculated using the values of the parameters listed in Table 1. On 14 decades of time, these curves fit the experimental results reasonably well.

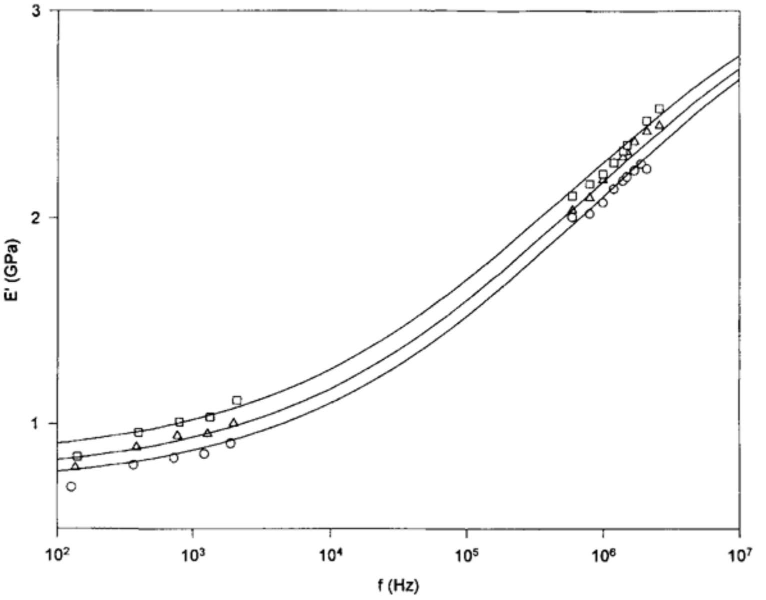


Fig. 7 Storage Young modulus obtained on the random copolymer (Eltex P KS409 from Solvay) stored ○ 2, △ 20 and □ 200 h at 30 °C. The full curves are calculated from Eqs. (1), (13), (14) and (22). The parameters are given in the upper part of Table 2

Table 2 Parameters for Eltex P KS409 from Solvay (random copolymer)

Parameter	Value	Unit
D_0	0.295	GPa^{-1}
D_1	1.825	GPa^{-1}
δ	0.4	–
A'	0.2	$\mathrm{s}^{-0.07}$
φ	0.07	–
D_b/τ_β^δ	160	$\mathrm{GPa}^{-1}\,\mathrm{s}^{-0.4}$
D_a	5.66	GPa^{-1}
μ	1	–
γ_0	0.305	–
χ	0.045	–

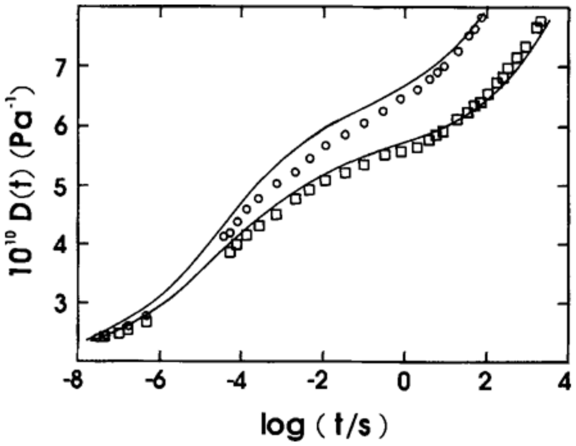


Fig. 8 Creep compliance obtained by Read et al. [9] on Propathene (ICI) stored ○ 2.5 and □ 216 h at 23 °C. For times shorter than a second, the compliance is calculated from dynamic data (ultrasonics, flexural and tensile resonance and tensile non-resonance) by using the Hamon's approximation. The full curves are calculated from Eqs. (8), (9), (12)–(15) and (21). The parameters are given in Table 1

Long term creep tests

Figure 9 deals with creep data obtained by Tomlins et al. [18] on iPP homopolymer (Royalite Propylex from VT Plastics) stored between 7 and 72 h at 23 °C. At times investigated, the β-process is completely relaxed; the creep compliance related to the lower glass transition reduces to

$$D_\beta(t) = D_0 + D_1 \; . \tag{23}$$

The theoretical curves, calculated from Eqs. (17), (21) and (23), are in very good agreement with the experimental results. The values of the parameters are reported in Table 3.

Creep results obtained at 30 °C on iPP random copolymer aged between 40 min and 75 days are plotted in Fig. 10. The theoretical full lines are expressed by Eqs. (18) and (21). In the former, the γ-exponent decreases with the storage time following a relation already proposed by Read et al. [9]

$$\gamma = \gamma_0 t_a^{-\chi} \tag{24}$$

where γ_0 and χ denote constants. Table 2 contains the values of the parameters.

Colloid & Polymer Science, Vol. 275, No. 2 (1997)

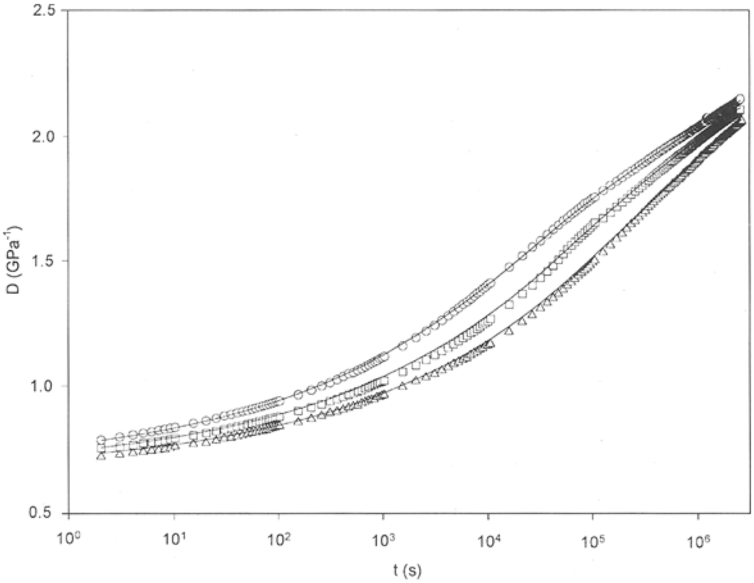


Fig. 9 Long-term creep compliance obtained by Tomlins et al. [18] on Royalite Propylex (VI Plastics) stored ○ 7, □ 24 and △ 72 h at 23 °C. The full curves are calculated from Eqs. (13), (14), (17), (21) and (23). The parameters are given in the upper part of Table 3

Table 3 Parameters for Royalite Propylex

Parameter	Value	Unit
$D_0 + D_1$	0.92	GPa^{-1}
$A'D_1$	0.2	GPa^{-1}s$^{-0.024}$
φ	0.024	
$A'D_a\,\tau_0^{\gamma(1-\mu)}$	0.44	GPa^{-1}s$^{-0.068}$
γ	0.22	
μ	0.8	

Discussion

The proposed simplified rheological model (Fig. 4) describes correctly dynamic and creep data obtained on various kinds of iPP, characterized by different crystallinity and molecular weights, in a wide frequency or time range covering up to 15 decades.

This model presents various advantages which are

1) Its broad range of application. This model can indeed be used in order to describe data corresponding to

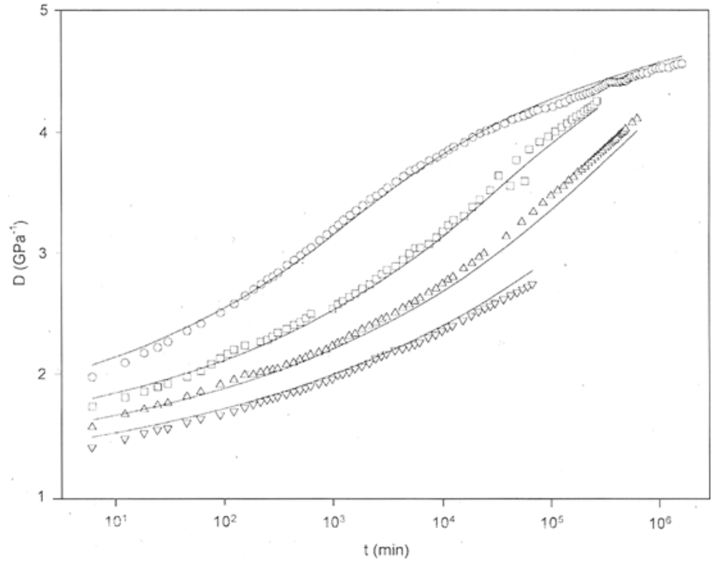


Fig. 10 Long-term creep compliance obtained on the random copolymer (Eltex P KS409 from Solvay) stored ○ 40 min, □ 20 h, △ 10 days and ▽ 75 days at 30 °C. The full curves are calculated from Eqs. (13), (14), (18), (21), (23) and (24). The parameters are given in Table 2

different kinds of loadings including dynamic spectroscopy, creep and relaxation (see [19]). It is also able to take effects like physical ageing and non-linearity (see [20]) into account. Moreover, it should be applicable for modelling the mechanical behaviour of other polymers, for example of amorphous polymers in a time window covering their glass transition and their secondary transition.

2) Its easy use in the time range covering the α-relaxation of iPP which results from 2 appropriate simplifications. The first one is due to the choice of a series association of the rheological elements related to both glass transitions. This choice is appropriate when the magnitude of the β-process is much lower than the magnitude of the α-process and when the time constants are strongly separated (by factor of $10^6 - 10^8$) [19]. The second simplification arises from the reduction of the Kelvin–Voigt element associated with the upper glass transition into a γ-element. This simplification is justified by the relatively short duration of the creep tests compared with the time constant of the α-relaxation.

3) The good fit for long-term creep tests performed on the homopolymers (see also [10]) and on the copolymer justifies the use of Eqs. (17) and (18), obtained by considering deformation as a diffusion process. This long-term agreement also supports, on one hand, the fact that the decrease of the β-fraction occurs on the behalf on an increase of the α-fraction and, on the other hand, the fact that the $\beta \rightarrow \alpha$ transformation occurs exclusively in the absence of mechanical stimulus.

4) The easy evaluation of the parameters which arises from the independence of both glass transitions. High frequency dynamic data give rise to the ageing time dependent magnitude of the β-process. This magnitude can then be introduced in the response associated to the α-process.

Moreover, the values obtained for the parameters are physically acceptable:

– The δ-exponent, characteristic of the width of the lower glass transition, is close to the value of 0.3 introduced by Read et al. [9] in a Cole Cole equation.

– The γ-exponent, related to the upper glass transition, is generally close to 0.25. This value is used by Read et al. [9] who described the α-relaxation with a Williams Watts function. In the case of the random copolymer, the decrease of the γ-exponent during ageing could mean that the deformation of the α-fraction of a strongly aged sample is harder than the deformation of a young one.

– Struik's parameter μ is generally close to 0.8 in the case of homopolymers. Read et al. [9] and Struik [21] find 0.77 and 0.7 respectively. The higher value obtained for the copolymer could arise from his greater sensitivity to physical ageing. This sensitivity is supported by the value of φ which reflects a faster $\beta \rightarrow \alpha$ transformation for the copolymer ($\varphi = 0.07$) than for homopolymers ($\varphi = 0.024$ and 0.0525).

Conclusion

A rheological model, composed of a modified Zener model in series with a γ-element allows a good description of dynamic and low strain creep data obtained on various iPP in a wide window of frequency or time covering the lower and the upper glass transitions. This model is also able to take into account the effects of physical ageing, i.e., an increase of the fraction of amorphous material relaxing in the α-range at the expense of the fraction of amorphous material relaxing in the β-range and an increase of the time constant of the upper glass transition which can proceed during creep experiments.

Acknowledgments The author wishes to thank Professor J.C. Bauwens for many discussions throughout the course of this work, Dr. N. Heymans for her helpful comments and suggestions related to the preparation of this paper and Mr. B. Triest for his efficient assistance in the experimental part of this work.

References

1. Boyer RF (1972) Seven Swinburn Award Address. The Plastic Institute, London
2. Takayanagi M (1963) Mem Fac Eng Kyushu Univ 23:1
3. Jourdan C, Cavaille JY, Perez J (1989) J Polym Sci Part B 27:2361
4. Boyd RH (1985) Polymer 26:323
5. Boyd RH (1985) Polymer 26:1123
6. Struik LCE (1987) Polymer 28:1521
7. Struik LCE (1987) Polymer 28:1534
8. Struik LCE (1982) Plast Rubb Proc Appl 2:41
9. Read BE, Dean GD, Tomlins PE (1988) Polymer 29:2159
10. Hellinckx S (1995) Coll Polym Sci 273:130
11. Bauwens JC (1992) Plast Rubb Proc Appl 18:149
12. Heymans N, Bauwens JC (1994) Rheol Acta 33:210
13. Heymans N, Private communication
14. Struik LCE, Physical ageing of amorphous polymers and other mateirals, Elsevier 1978
15. Read BE, Dean GD (1978) The determination of dynamic properties of polymers and composities, Adam Hilger Ltd
16. Read BE, Dean GD, Duncan JC (1991) Determination of elastic and mechanical properties, J. Wiley & Sons
17. Hamon BV (1952) Proc Int Elec Engrs 99 point IV
18. Tomlins PE, Internal report of the European Technical Committee
19. Heymans N, accepted in Rheological Acta
20. Hellinckx S (1995) Doctoral Thesis, Université Libre de Bruxelles
21. Struik LCE (1989) Polymer 30:799