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ORIGINAL CONTRIBUTION

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# A quantitative model describing physical aging in isotactic polypropylenes

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**Abstract** Physical aging of isotactic polypropylenes (homopolymer and random ethylene-propylene copolymer) at room temperature is investigated by low-strain creep, damping measurements, differential scanning calorimetry, and infra-red spectroscopy. Examination of the results suggests that physical aging produces a decrease of the magnitude of the $\beta$-relaxation (lower glass transition) and an increase of the magnitude and of the relaxation time of the $\alpha$-relaxation (upper glass transition). A model is proposed that accounts for the variations of the fractions of amorphous material which undergo these relaxations. In this model, deformation and increase in the $\alpha$-fraction at the expense of the $\beta$-fraction are expected to be diffusion processes. The agreement with experimental data is good. Moreover, the $\alpha$-form is shown to be an amorphous phase rich in molecular segments having a helical conformation.

**Key words** Isotactic PP – physical aging – low-strain creep – magnitude of $\beta$ and $\alpha$ relaxations – amorphous forms

## Introduction

The phenomenon of physical aging in amorphous glassy polymers has been widely covered in the literature. This aging, observed at temperatures below $T_g$, has been explained in terms of a decrease in free volume and in segmental mobility [1] or a decrease in structural temperature [2–4]. In both cases, kinetics of aging have been proposed.

Also, semicrystalline polymers are in a non-equilibrium state and undergo aging, not only below, but also above their glass transition temperature. One of the most used models describing the aging in semicrystalline polymers has been proposed by Struik [5–6]. According to this model, the crystals disturb the amorphous phase and reduce the mobility in their vicinity. The main consequence of this consists in an extension of the glass transition towards the high-temperature side. Therefore, even above the $T_g$ of the bulk amorphous material, some parts of the amorphous phase are glassy and undergo aging.

For isotactic polypropylene (iPP), of which $T_g$ (also called $\beta$ transition) lies around 275 K, aging effects have been detected over a wide range of temperatures (from 170 to 370 K) [7]. In particular, the consequences of storage at room temperature were investigated. Struik's measurements on the linear thermal expansivity [7] shows two transitions: the first one, situated around 0 °C which corresponds to the $\beta$ relaxation, and the second one (also called $\alpha$) around 310 K. The magnitude of $\alpha$ increases when storage time at room temperature becomes longer and the position of $\alpha$ shifts towards higher temperatures when aging temperature is raised. According to Struik, this $\alpha$ process, corresponding to the upper glass transition, involves motions of restrained amorphous segments. The aging effects have then been interpreted in terms of increases in retardation times for both the $\beta$ and the $\alpha$ processes giving rise to horizontal shifts of the creep curve along the log time axis.

However, Read and coworkers [8] have shown that aging in iPP could modify the magnitude of both relaxations rather than the retardation times. According to their model, where the distribution of the relaxation times has been obtained from a generalized Voigt model by integrating over a Cole-Cole relaxation function for the $\beta$-range and a Williams-Watts function for the $\alpha$-range, the magnitudes of both relaxations decrease with elapsed time. At creep times longer than 1 day, the response of this model diverges from the experimental results.

The purpose of this paper is to propose a model which accounts for the changes, due to aging, in both magnitudes and relaxation times for creep times on the order of 3 months. The model is in agreement with the creep measurements of Read et al., as well as with our data. Moreover, the theoretical changes in the relaxations magnitudes were compared with data obtained from dynamic mechanical analysis and from infra-red spectroscopy; the results are promising.

## Experimental

### Material

Two commerically-available isotactic polypropylene (iPP) were used: a homopolymer (Eltex P HS200 from Solvay) and an ethylene-propylene random copolymer (Eltex P KS409 from Solvay), both supplied as extruded sheets 1 or 2 mm thick. Since the molecular weights of both kinds of samples are close to each other, the main difference lies in their crystallinity which is reduced by a factor of 2 by the presence of 2–3% ethylene in the copolymer.

The tensile creep specimens of KS409 were dumbbell shaped with a gauge length of 80 mm and a $17 \times 2$ mm$^2$ cross-section.

### Thermal pre-treatments

In order to erase the previous aging effects [7–8], annealing of the PP KS409 samples used in the creep and damping tests was performed at 373 K for 4 h. Cooling to 303 K (the aging temperature) was realized by quenching the samples in ice-water before putting them in an environmental chamber at 303 K.

### Creep tests

Tensile creep tests have been performed at 303 K on samples of PP KS409 aged between 2 h and 10 days at 303 K. Dead-weight loading was used inside an environmental chamber. Strain was measured with a linear velocity transducer at short times or with a dial gauge at longer times.

### Damping tests

Internal friction was measured on aged PP KS409 samples as a function of temperature between 225 and 375 K using a torisonal Metravib low frequency microanalyzer. The testing frequency and the heating or cooling rate were equal to 1 Hz and 60 K/h respectively. The aging temperature was 303 K and the aging times were included between 2 h and 40 days.

### Differential scanning calorimetry

Measurements were made with a Perkin-Elmer DSC-2C calorimeter at a fixed heating rate of 20 K/min from 230 to 360 K. The samples of PP HS200 and PP KS409 used throughout the DSC tests were annealed at 373 K for 1 h in the calorimeter and cooled to 230 K at 320 K/min with or without intermediate aging at 303 K.

In order to check that annealing at 373 K erases previous aging, a DSC measurement was performed on a sample of copolymer quenched from the melt in the calorimeter (cooling rate of 320 K/min). the thermogram obtained between 220 and 350 K is very similar to the one related to a sample quenched from 373 K.

### Infra-red spectroscopy

For IR spectroscopy, films of PP KS409 were prepared by melting them in a hot press (at a temperature of 430 K) between two polytetrafluorethylene plates. Pressure was applied during a short time to reduce the thickness of the samples. The films were then quenched in an ethanol–liquid nitrogen mixture (at a temperature close to 220 K). Samples were then allowed to warm to room temperature. The IR spectra between 800 and 1020 cm$^{-1}$ were taken at room temperature on a Perkin-Elmer 1725X FTIR spectrometer at elapsed times between 3 min and 6 days.

## Results

The results of DSC measurements performed on PP HS200 and PP KS409 quenched from 373 K or aged 5 h at 303 K are shown in Figs. 1a and 1b, respectively. It can be seen that the magnitudes of the relaxations associated to the amorphous phase (i.e., the $\beta$ and the $\alpha$ relaxations corresponding to the lower and the upper glass transitions, respectively) are greater in the case of PP KS409, which results from the lower crystallinity of the copolymer. Therefore, throughout this paper, the influence of physical aging on both relaxation magnitudes is mainly investigated for the copolymer. Moreover, the magnitude of the $\beta$ relaxation (around 265 K) decreases when aging time increases and the $\alpha$ relaxation (around 320 K) does not appear on the thermogram related to the PP KS409 quenched sample (curve A of Fig. 1b).

The damping curves related to samples of PP KS409 aged 2 h and 12 days at 303 K are reported in Fig. 2. The height of the $\beta$ peak (around 275 K) decreases when the aging time is raised. On the other hand, the magnitude of the large peak observed at higher temperatures does not seem to be affected by a storage at 303 K.

Figure 3 represents the damping curve obtained on cooling a sample of PP KS409 pre-annealed 1 h at 373 K in the low-frequency analyzer. This curve shows then the magnitudes of the relaxations related to an unaged sample. For comparison, the curve obtained on heating a sample aged 2 h is also drawn. It can be seen that the height of the peak around 335 K, which was independent of aging time in measurements performed on heating (because the measurement itself gave rise to an additional thermal treatment); (see Fig. 2), is smaller than in the heating test.

The difference between two IR spectra related to PP KS409 films aged 24 h and 3 min is plotted in Fig. 4.

**Fig. 1** a) DSC scans of PP HS200 at a heating rate of 20 K/min after different thermal histories: A) 1 h at 373 K, cooled to 230 K at 320 K/min; B) 1 h at 373 K, cooled to 303 K at 320 K/min, 5 h at 303 K, cooled to 230 K at 320 K/min. b) Idem for PP KS409

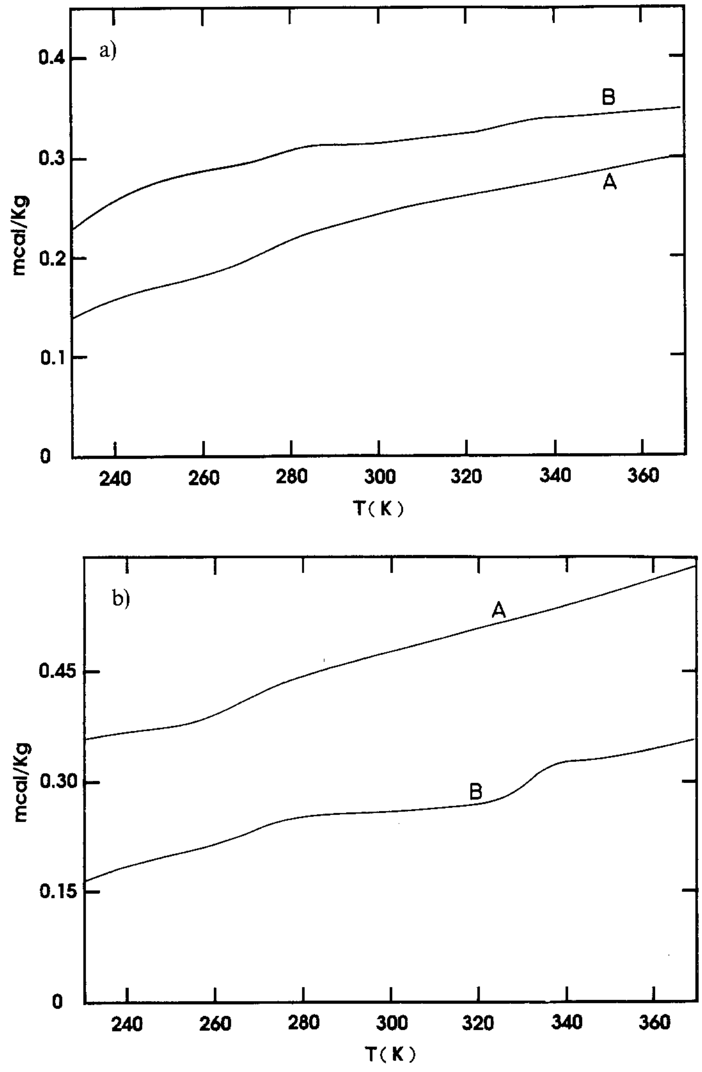
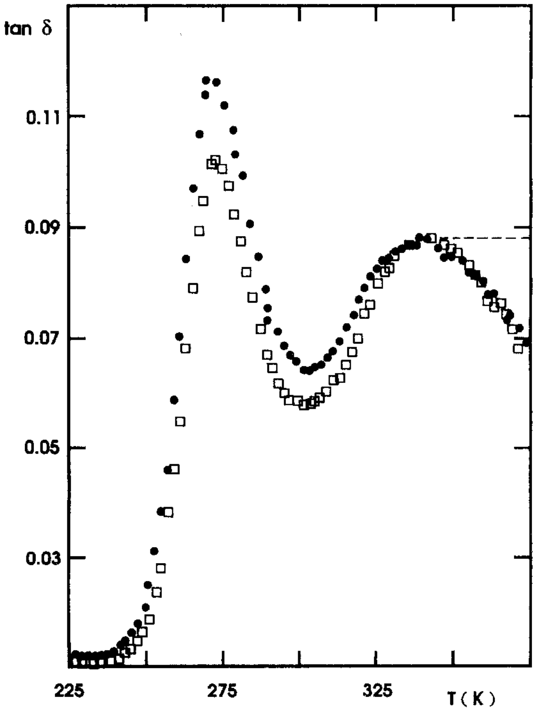


**Fig. 2** Loss curves obtained on PP KS409 samples aged ●: 2 h and □: 12 days at 303 K after annealing for 4 h at 373 K. The curves are related to the same frequency, 1 Hz, and the same heating rate, 60 K/h



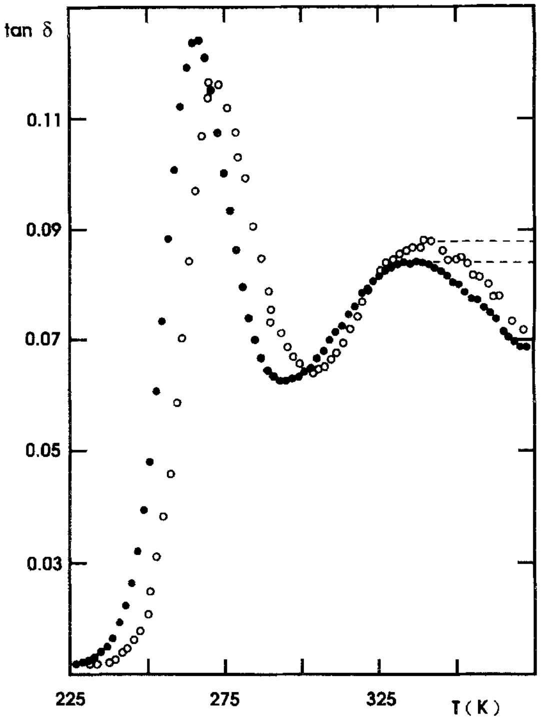


**Fig. 3** Loss curves obtained at a frequency of 1 Hz ●: on cooling a sample of PP KS409 at 60 K/min after annealing 1 h at 373 K and ○: on heating a sample of PP KS409 at 60 K/min after storage at 303 K for 2 h

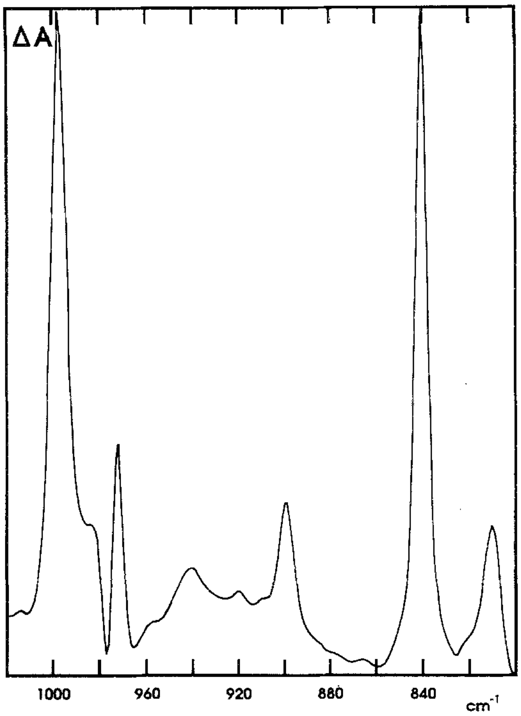


**Fig. 4** Difference spectrum obtained by subtracting the absorbance spectrum of a PP KS409 film aged 3 min from that of a film aged 24 h ($\Delta$A represents the difference of both absorbances expressed in arbitrary units). The aging was performed at room temperature after quenching from the melt

Between 800 and 1020 $\mathrm{cm}^{-1}$, two absorbance peaks are influenced by the age of the sample. They are situated around 842 and 998 $\mathrm{cm}^{-1}$.

## Model

The model consists in a modification of a model proposed earlier in this laboratory [9] in order to take aging effects into account.

In the original model, a constant stress is applied to a deformed polymeric chain where (k-1) elements are strained. The average number of steps required to deform the $k^{\mathrm{th}}$ element is $k^n$ and the corresponding time is $k^n\tau_0$ where $n$ and $\tau_0$ denote the order of the diffusion process and the time constant of one step, respectively. The resulting retarded strain increase is

$$d\varepsilon_r = \varepsilon_0 \frac{dt}{k^n \tau_o}, \tag{1}$$

where $\varepsilon_0$ is the strain of one element. Since $\varepsilon_r = k\varepsilon_0$ and taking $\tau = \tau_0/\varepsilon_0^{n+1}$, the differential equation related to the retarded extension becomes

$$d\varepsilon_r = \frac{1}{\varepsilon_r^n}\frac{dt}{\tau(t_a, T)}. \tag{2}$$

This model is able to describe the non-linear behavior and to take rejuvenation and aging effects into account [10]. In these cases, the retardation time depends on the applied stress, the structural state of the polymer, and the aging time, respectively.

In this paper, non-linear-behavior and structural modification induced by large deformation are not studied. Only the aging effects are considered; they can be simply expressed by assuming that the characteristic time increases with aging time following

$$\tau = \tau_0(T)\left(\frac{t_a}{\tau_1}\right)^{\mu}, \tag{3}$$

where $\mu$ is Struik's exponent [1] (between 0.7 and 0.8 in the case of iPP [11–12]). If aging continues during creep, the total aging time is $t + t_a$ and the creep equation (2) becomes

$$d\varepsilon_r = \frac{1}{\varepsilon_r^n}\frac{d(t/\tau_0)}{[(t + t_a)/\tau_1]^{\mu}}. \tag{4}$$

Integration of this equation gives

$$\varepsilon_r = A[(t + t_a)^{1-\mu} - t_a^{1-\mu}]^\gamma \,, \tag{5}$$

where $\gamma$ has been substituted for $1/1 + \mathrm{n}$ and where $\mathrm{A} = [\tau_1^\mu/(\gamma\tau_0(1-\mu)]^\gamma$.
In the early stages of creep, no aging effects appear since $t \ll t_a$ and the equation of the creep curve, resulting from integration of Eq. (4), is a power-law with exponent $\gamma$

$$\varepsilon_r = \left[\frac{\tau_0}{\gamma(\frac{t_a}{\tau_1})^\mu}\right]^\gamma t^\gamma \,. \tag{6}$$

Very short-term creep measurements performed by Read et al. [8] have shown that the relaxed compliance of the $\beta$ relaxation decreases when aging time increases. This feature can be explained by considering that the fraction of the amorphous phase which relaxes in the $\beta$-range decreases with increasing aging times. This decrease of the fraction of "$\beta$-form", already suggested by Vittoria [13], might be accompanied by an increase in the amorphous fraction undergoing the $\alpha$ relaxation (the "$\alpha$-form") since no increase in crystallinity is observed [14, 15].

This assumption is in agreement with the results obtained from differential scanning calorimetry (see Fig. 1) and from damping tests (see Figs. 2 and 3). Indeed, the magnitudes of the specific heat step and of the tan $\delta$ peak, associated with the $\beta$ process, both decrease when storage time at 303 K is raised (see Figs 1 and 2, respectively). Moreover, no $\alpha$ relaxation is observed in the thermogram related to the quenched sample (see Fig. 1) and the height of the wide peak centered around 335 K is the lowest when damping is measured on cooling a sample annealed 1 h at 373 K.

These variations of the fractions of both forms can be modeled assuming that an equation similar to the creep equation (4) can be used to describe the increase in the fraction of "$\alpha$-form" during storage at room temperature:

$$d\alpha = \frac{1}{\alpha^n}\frac{d(t/\tau_0)}{(t_a/\tau_1)^\mu} . \tag{7}$$

Integration of which gives

$$\alpha = A' t_a^{\gamma(1-\mu)} \,. \tag{8}$$

Then, if the same diffusion process is responsible both for creep and for the increase in the fraction of "$\alpha$-form", exponents $\gamma$ and $\mu$ appearing in Eqs. (5) and (8) should be identical. In this case, the creep equation in the $\alpha$-range, obtained by multiplying the retarded extension (Eq. (5)) by the $\alpha$-fraction (Eq. (8)), is

$$\varepsilon_{r\alpha} = AA' t_a^{\gamma(1-\mu)}[(t + t_a)^{1-\mu} - t_a^{1-\mu}]^\gamma . \tag{9}$$

The corresponding creep compliance is

$$J_{r\alpha} = C t_a^{\gamma(1-\mu)}\,[(t + t_a)^{1-\mu} - t_a^{1-\mu}]^\gamma \tag{10}$$

## Comparison of the model with the data

### Tensile creep experiments

Equation (10) is compared in Fig. 5 with Read et al.'s results obtained on iPP homopolymer stored at room temperature for aging times between 8 and 72 h prior to the creep test. The theoretical curves were obtained taking $\gamma = 0.25$, $\mu = 0.8$ and $\mathrm{C} = 3.63.10^{-10}\mathrm{Pa}^{-1}\mathrm{s}^{-0.1}$. A vertical shift was applied to the calculated curves to take into account the retarded compliance related to the $\beta$ relaxation. This shift was calculated from the equation obtained by Read et al. (from creep tests performed at times shorter than 10s) for the $\beta$ relaxation magnitude

$$J_\beta = B t_a^{-k} + J_{u\beta} \,, \tag{11}$$

where the unrelaxed compliance $J_{u\beta} = 2.10^{-10}\,\mathrm{Pa}^{-1}$, $\mathrm{k} = 0.04$ and $\mathrm{B} = 5.94.10^{-10}\,\mathrm{Pa}^{-1}\,\mathrm{s}^{0.04}$.

The agreement of our model is good in the whole time range investigated. In particular, at long times, the theoretical curves fit the experimental data better than Read's description. In the short time range, however, it can be seen that the curves lie above the experimental values. This feature is due to the vertical shift $J_\beta$ applied to the curves which represents the total creep compliance related to the $\beta$ process when this relaxation is completed. Therefore, at short times, this shift overestimates the real compliance associated with the $\beta$ process which is still relaxing.

In Fig. 6, the response of our model (Eq. (10)) is compared with our creep data obtained at 303 K on the

**Fig. 5** Long-term creep compliance of PP homopolymer. The data, related to aging times at room temperature of □: 8 h, △: 24 h; ○: 72 h, are taken from ref. [8]. The curves are calculated from Eq. (10) with $\gamma = 0.25$, $\mu = 0.8$ and $\mathrm{C} = 3.63.10^{-10}\,\mathrm{Pa}^{-1}\,\mathrm{s}^{-0.1}$ and are shifted following Eq. (11) with $J_{u\beta} = 2.10^{-10}\,\mathrm{Pa}^{-1}$, $k = 0.04$ and $\mathrm{B} = 5.94.10^{-10}\,\mathrm{Pa}^{-1}\,\mathrm{s}^{0.04}$

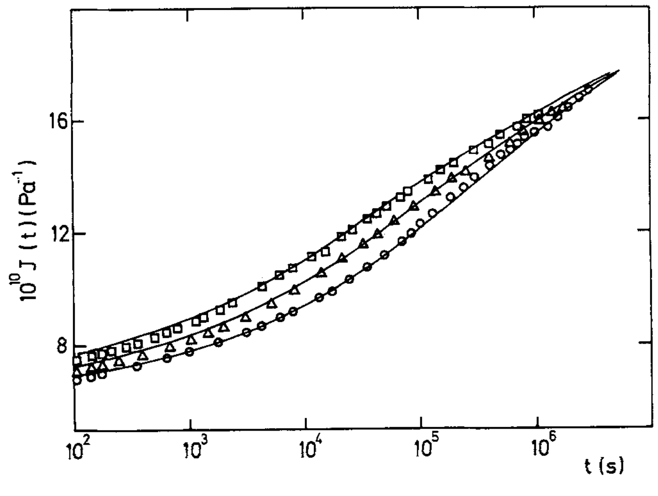
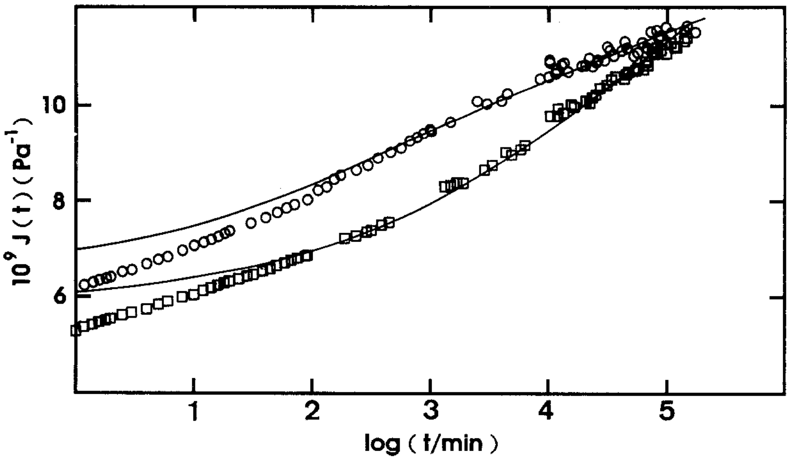


Fig. 6 Long-term creep compliance of PP KS409 aged ○: 280 min; □: 10 days at 303 K after annealing at 373 K for 4 h. The curves are calculated with Eq. (10) with $\gamma = 0.25$, $\mu = 0.76$ and $C = 2.10^{-9}\,Pa^{-1}\,min^{-0.12}$



copolymer aged 280 min and 10 days at 303 K before testing. The best fitting parameters are $\gamma = 0.25$, $\mu = 0.76$ and $C = 2.10^{-9}\,Pa^{-1}\,min^{-0.12}$. The calculated curves were shifted vertically following

$$J_\beta = J_{\beta 0}(1 - B' t_a^m)\,, \tag{12}$$

where the $\beta$ magnitude without aging $J_{\beta 0} = 8.55.10^{-9}\,Pa^{-1}$, m = 0.06 and B' = 0.19 $min^{-0.06}$.

The explanation for the disagreement between the curves and the experimental results at short times is the same as above. At longer times, the present model gives a good description of low strain creep of iPP.

## Damping tests

In the proposed model, the fraction of "α-form" is assumed to increase with aging time, following a power-law (see Eq. (8)). Moreover, since no change in crystallinity is observed [14, 15], this increase in the "α-form" quantity occurs at the expense of the $\beta$ fraction. Thus,

$$\beta = 1 - A' t_a^{\gamma(1-\mu)}\,. \tag{13}$$

Therefore, the fraction of the "$\beta$-form" is expected to decrease according to Eq. (13) until the irreducible $\beta$ fraction is reached.

The fraction of the "$\beta$-form" can be determined from the height of the $\beta$ peak obtained in damping tests (see Fig. 2). In Fig. 7, this height is plotted versus $t_a^{0.06}$ for PP KS409 samples aged at 303 K between 2 h and 40 days. The particular value of the exponent $\gamma(1 - \mu)$ of 0.06 corresponds to $\gamma = 0.25$ and $\mu = 0.76$, i.e., values identical to those used previously in the modeling of creep of PP KS409. It can be seen that the fraction of "$\beta$-form" follows the prediction of the model and exhibits the expected cutoff at long times.

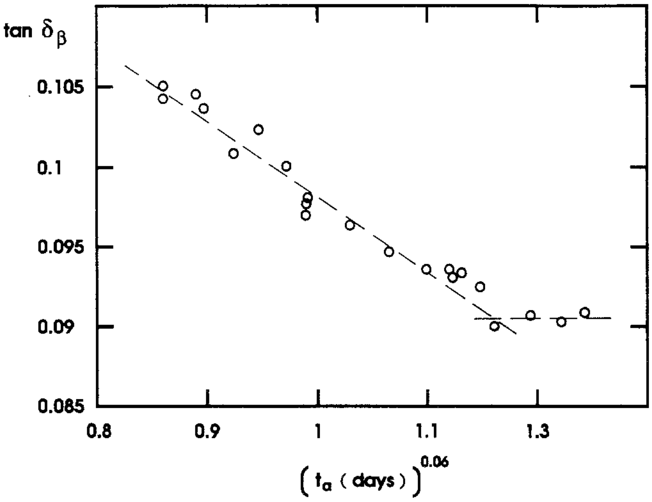


**Fig. 7** Decrease of the height of the $\beta$ damping peak of samples of PP KS409 aged at 303 K versus aging time. The reported heights of the peak result from the subtraction of the tan$\delta$ value related to the minimum in the damping curves around 230 K from the tan$\delta$ value at the maximum of the $\beta$ peaks. The value of exponent $\gamma(1 - \mu)$ of the aging time corresponds to the same values of parameters $\gamma$ and $\mu$ as used previously in the PP KS409 creep experiments (see Fig. 6)

## Infra-red spectroscopy

Figure 4 shows that the absorbance peaks situated at 842 and 998 $cm^{-1}$, resulting from vibrations in chain segments which have a helical structure [16], grow with aging time.

The height of such peaks, normalized by the absorbance at 973 $cm^{-1}$ (the magnitude of which seems to be independent of the conformation [17]), is plotted against $t_a^{0.06}$ in Fig. 8. The helical content increases linearly with $t_a^{0.06}$ in agreement with the proposed model (see Eq. (8)) since the "α-form" is assumed to be an amorphous phase rich in molecular segments having a helical conformation.

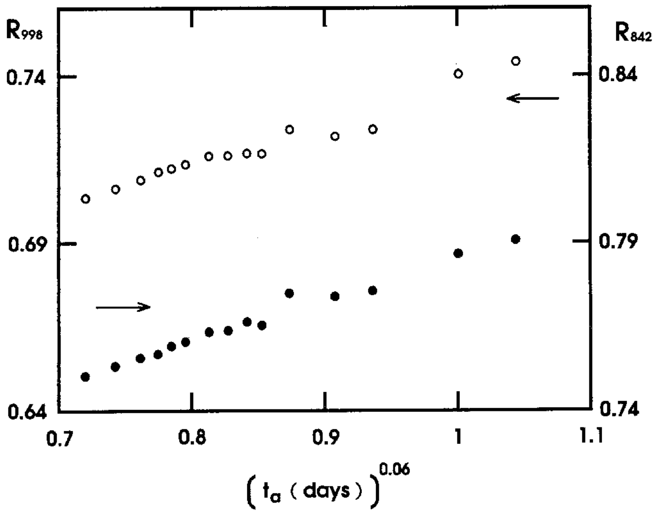


**Fig. 8** Ratios $R_{842}$ and $R_{998}$ of the heights of the peaks at ●: 842 and ○: 998 $cm^{-1}$ to the one at 973 $cm^{-1}$ for PP KS409 films aged at room temperature versus the aging time. Before aging, the samples were quenched from the melt. The value of the exponent $\gamma(1-\mu)$ of the aging is the same as Fig. 7

## Discussion

The proposed model is in agreement with creep, dynamic mechanical and infrared data. In particular, in the case of creep measurements performed on PP copolymer, a vertical shift, which reflects the contribution of the $\beta$ process to the creep compliance, is applied to the curves calculated from Eq. (10). This shift, which has been determined experimentally, is proportional to the $\beta$ fraction expressed by Eq. (13).

The values of the parameters $\gamma$ and $\mu$ used in the modeling of homopolymer (results from [8]) and copolymer creep results are close to those mentioned in the literature. The value $\gamma = 0.25$ was also found by Read et al. [8] to give a good description of short time creep in iPP in the $\alpha$-range and is close to the values of 0.29 and 0.25 found by Struik at 296 and 313 K, respectively [12]. Moreover, the value $\mu = 0.8$ is equal to the one obtained by Struik [12] at 296 K in the case of low strain creep tests of iPP. Struik's creep experiments performed at 313 K lead to a smaller $\mu$ value of 0.75 [12]. Therefore, the only really adjustable parameter in Eq. (10) is the front factor $C$.

The comparison of the model with the experimental results has shown that the deformation, induced by creep, and the increase of the amount of "$\alpha$-form", due to storage at room temperature, can both result from diffusion processes. Since the values of $\gamma$ and $\mu$ are equal in both cases, these processes are characterized by the same order ($n = 3$) and their relaxation times increase with aging time in the same way. Identical diffusion processes could therefore be responsible for deformation and for aging.

Such similarities have also been found for amorphous polymers [18]. In this case, the evolution of the structural temperature with aging time was calculated through the WLF deformation relation with universal constants written as a function of the structural temperature. The result predicts that, at a constant aging temperature, each increase in the aging time by a factor to 10 causes a decrease of the structural temperature by 3 K. Since the enthalpy relaxation occurring during aging is proportional to the structural temperature change (the coefficient of proportionality being the specific heat drop $\Delta C_p$ related to the glass transition), the enthalpy relaxation magnitude must be multiplied by $3\Delta C_p$ when the aging time is increased by a factor of 10. Experimental results have confirmed this feature which showed that aging produces similar structural changes as does deformation in amorphous polymers.

## Conclusions

1) Physical aging of iPP (homopolymer and random copolymer) around room temperature consists, on one hand, in an increase in the retardation times of the $\alpha$-process and, on the other hand, in an increase of the fraction of amorphous material which relaxes in the $\alpha$ range. This increase of the amount of the "$\alpha$-form," which contains more helical structural than the "$\beta$-form," occurs at the expense of the latter.

2) A model has been proposed in order to account for these features. In this model, deformation and change in the $\alpha$ fraction are expected to be diffusion processes. The agreement with the experimental data is good. Moreover, the order of the diffusion processes and the dependence of their relaxation time on aging are found to be equal in both cases.

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