Physical Aging of Drawn Polypropylene Fibers

C. P. BUCKLEY* and M. HABIBULLAH,** *Department of Textile Technology, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England*

Synopsis

Drawn fibers of polypropylene have been shown to undergo spontaneous stiffening during storage for several weeks at room temperature after being quenched from higher temperatures below the melting region. The effect occurs in both drawn and undrawn fibers and does not depend on the details of heat treatment prior to the quench. Stress relaxation and density data are in quantitative agreement with an explanation in terms of a gradual collapse of free volume during storage. The effect appears to be identical to "physical aging" previously observed in isotropic molded samples of polypropylene.

INTRODUCTION

During a study of heat setting of synthetic fibers, we have found that drawn polypropylene fibers when quenched to room temperature from temperatures below the melting region undergo a remarkable spontaneous stiffening during subsequent storage at room temperature. The purpose of this article is to report measurements of the effect for storage over several weeks and to present evidence relating to its origin.

Such effects have been observed before in polymeric solids[1-16] and indeed in other substances.[13] Fibers of wool[17-20] and nylon[19,20] show a similar phenomenon when their water content is suddenly reduced. The behavior to which we refer is thermally reversible and of purely physical origin (distinct from chemical effects such as photochemical degradation). Struik has therefore termed it "physical aging."[13]

Drawn polypropylene (PP) fibers are of special interest in this context for two reasons. Firstly, physical aging is of great practical importance for these fibers since it is especially pronounced at room temperature in PP, and sudden cooling to room temperature is a common feature of textile operations such as texturing of yarns and heat setting of fabrics. Secondly, they offer an opportunity to choose between two proposed mechanisms for physical aging, either of which might reasonably be expected to apply in this case. They are as follows. (a) Aging corresponds to densification of the noncrystalline fraction, in the manner of an amorphous polymer at temperatures just below the glass transition,[2] but shifted to higher temperatures by the local constraint on noncrystallized molecular segments exerted by crystals.[13,15] (b) Aging corresponds to delayed recrystallization of noncrystalline segments generated during constant length heating of a drawn polymer to temperatures where otherwise it would shrink,

* Present address: Department of Mechanical Engineering, UMIST, Manchester M60 1QD, U.K.
** Present address: Department of Mechanics and Materials Science, Rutgers State University, P.O. Box 909, Piscataway, NJ 08854, U.S.A.

as proposed for highly drawn fibers of polyethylene.[12,21]   The present experiments were *inter alia* designed to test the validity of (a) and (b) for drawn fibers of PP.

EXPERIMENTAL

It became necessary in the present work to compare PP filaments in oriented and unoriented states.   We therefore studied two batches of specimens, both manufactured from the same grade of PP (ICI Propathene GWE 27) by melt extrusion at 220°C, but prepared with and without subsequent drawing.   Fiber A was a monofilament drawn at 120°C to a draw ratio of 8, with a diameter and birefringence of 129 μm and $(3.28 \pm 0.08) \times 10^{-2}$, respectively.   Fiber B was a single filament taken from a multifilament yarn and studied as spun.   Its diameter and birefringence were 310 μm and $(5.27 \pm 0.02) \times 10^{-4}$, respectively.

The filaments were stored in a temperature- and humidity-controlled laboratory at 20 ± 1°C and 65 ± 2% RH, in the dark, for several months prior to use. They were then subjected to the following thermal sequence: 12-cm fiber samples were plunged into silicone oil at a temperature T_a, where they were held for a time t_a, either unconstrained to allow free shrinkage (FS) or constrained to maintain constant length (CL), and then removed and immediately quenched into silicone oil at 20°C.   After being removed from the oil (and, if clamped, after being released), samples were stored at 20°C and tested in tensile stress relaxation at various times t_e, measured from the moment of the quench.   The thermal history of the samples from their arrival in the laboratory up to the initiation of a particular stress relaxation test may therefore be summarized by the scheme

$$20 \uparrow T_a(t_a, \text{ FS or CL}) \downarrow 20(t_e)$$

where an arrow up or down represents a temperature jump up or down.

The purpose of the experiments was to study changes in fiber properties caused by thermal history alone, without any effects being introduced by the repetitive application of strain.   It was therefore essential to carry out all stress relaxation tests in the linear viscoelastic region, i.e., at small strains.   The tests therefore required particular care to achieve results of satisfactory precision, and we describe the procedure in some detail.

They were carried out using an Instron tensile testing machine on samples with a nominal gauge length of 10 cm, which were rapidly loaded and unloaded in stress relaxation experiments by applying a cross-head velocity of 50 cm/min. The duration of stress relaxation, t_r, was always chosen so that $t_r \ll t_e$ and was routinely chosen to be 10 s, while the tensile strain applied was always ca. 3 $\times$ 10^{-3} or less, where the present fibers were linear viscoelastic to within the precision of measurement.   A recovery time of at least $10t_r$ was allowed between consecutive tests on the same specimen.   To ensure that the fiber was taut at the start of each test, a small prestrain of ca. 5×10^{-4} was applied at a time many times greater than t_r before the start, and its associated stress relaxation curve was linearly extrapolated to provide the baseline for the test.   Two further precautions were taken.   Cross-head displacement was measured using a dial gauge; and the gauge length was defined, without causing excessive damage to the sample in clamping, by securely gluing its ends onto pieces of stainless steel

shim, which were then clamped in the jaws of the machine. The gauge length and fiber diameter were measured for each sample using a cathetometer and optical microscope with eyepiece graticule, respectively.

Results are presented here chiefly as the 10-s isochronal tensile stress relaxation modulus $E(10 \text{ s})$, but also include two longer-term relaxation tests for large values of t_e. Applying the above procedures it was found that $E(10 \text{ s})$ was reproducible (for a given thermal history) to within ca. 1% for separate measurements on the same fiber sample—including removal and reclamping in the testing machine. Reproducibility between different samples with the same history was better than this. In most cases, two samples were prepared, for any particular thermal history, and one sample was tested less frequently than the other. The purpose was to check the reproducibility of the measurements and especially to confirm that these were not affected by the repetitive testing during aging.

The physical aging which emerged from the mechanical tests was studied further in two subsidiary experiments. The first of these was density measurement, achieved using a density gradient column of toluene and carbon tetrachloride.* Values of density ρ were reproducible to within $2 \times 10^{-4} \text{ g/cm}^3$. The second was the study of melting by differential scanning calorimetry (DSC), using a Perkin–Elmer DSC2, with samples of ca. 2 mg and a heating rate of 20°C/min. The latent heat of fusion ΔH was determined with a reproducibility of ca. 2.5%.

RESULTS AND DISCUSSION

DSC studies of the present samples showed that melting began within the range 126–134°C (the precise value depending on thermal history). To ensure that premelting did not intervene during heat treatment, values of T_a below this range were chosen, and samples of fiber A were subjected to thermal histories of the form $20 \uparrow T_a(15 \text{ s}, \text{CL}) \downarrow 20(t_e)$.

Resulting values of $E(10 \text{ s})$ during the ensuing ten weeks of storage at 20°C are plotted versus t_e in Figure 1, where the original modulus $E(10 \text{ s})$ (prior to heat treatment) is also indicated as the "previous value." Heat treatment can be seen to cause a significant decrease of $E(10 \text{ s})$, as measured at short times t_e, the effect increasing with increasing T_a. But then, during storage of the sample at 20°C, $E(10 \text{ s})$ rises steadily toward its original value, surpassing it within 10^5 min in two of the three cases shown. Physical aging is thus clearly apparent in these samples, with the isochronal modulus increasing approximately proportionately to $\log t_e$ over four decades of t_e. It is interesting to note the large magnitude of the increase. For example, $E(10 \text{ s})$ for the samples with $T_a = 120°C$ increases by 60% between $t_e = 10$ min and $t_e = 10^5$ min. These data show that physical aging of drawn fibers of PP is as pronounced as that of isotropic molded samples of PP.[3,13–15] It therefore needs to be taken into account in the storage of PP fibers following any manufacturing process involving quenching, *even from temperatures below the melting range.*

When we look for the physical mechanism of aging in drawn PP, we face a

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* For optimum thermal stability, the temperature gradient column was controlled at 23°C. There was therefore a small discrepancy in the rates of aging between samples in the column and those stored at 20°C. From the results of Struik,[15] however, this may be shown to introduce an error which is negligible compared with those from other sources.
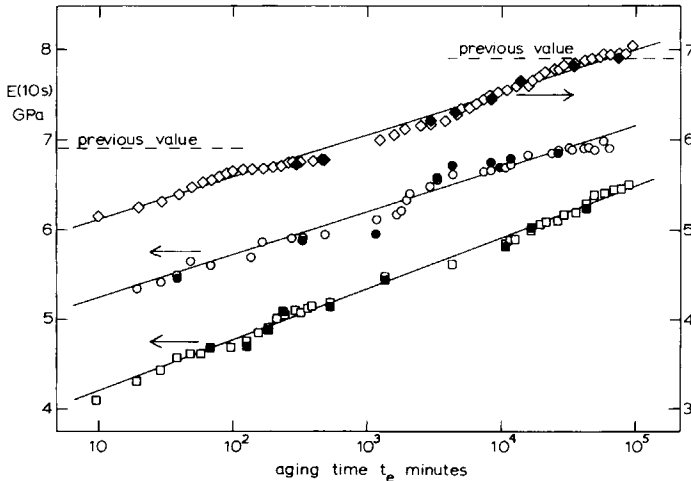
Fig. 1. Isochronal stress relaxation modulus $E(10\ s)$ vs. t_e during aging of fiber A after heat treatment for 15 s at constant length: ($\Diamond$ and $\blacklozenge$) $T_a = 80°C$; ($\bigcirc$ and $\bullet$) $T_a = 100°C$; ($\square$ and $\blacksquare$) $T_a = 120°C$.

dilemma. On the one hand, the results are consistent with those obtained on isotropic PP by other authors,[3,13–15] explained qualitatively by Struik[13] in terms of spontaneous densification of the noncrystalline fraction. On the other hand, the results also resemble the spontaneous stiffening of highly drawn linear polyethylene following a heat treatment at constant length,[12] which was explained in terms of slow recrystallization at room temperature.[12,21] Further experiments were conducted to explore the applicability of these previous explanations to the case of drawn fibers of PP.

The recrystallization mechanism proposed by Arridge, Barham, and Keller[12] and Peterlin[21] relies on the generation of new noncrystalline material by the "stripping off" of some molecular segments from crystals, by the entropic force generated by intercrystalline tie segments during heating at constant length. During unconstrained heating, these internal forces instead generate shrinkage of the fiber. This mechanism therefore predicts that aging will be absent, or at least much reduced, in samples allowed to freely shrink during heating. Arridge et al.[12] did not, however, report whether this was so for their material.

This point was checked for drawn PP by subjecting samples of fiber A to thermal histories of the form $20 \uparrow T_a(15\ s, FS) \downarrow 20(t_e)$. Figure 2 shows the resulting values of $E(10\ s)$ versus t_e for $T_a = 100$ and $120°C$. Similar results were obtained with other combinations of T_a and t_a. It is clear from Figure 2 that physical aging is as pronounced for these samples as it is for the CL samples. The main difference between Figures 1 and 2 is that free shrinkage can be seen to cause a larger decrease of the modulus $E(10\ s)$ for given T_a, t_a, and t_e. The recrystallization mechanism proposed by Arridge et al.[12] and Peterlin[21] cannot, therefore, apply to the present samples. This point was confirmed by the occurrence of aging even in undrawn fibers. To illustrate this, samples of fiber B were subjected to similar thermal histories. Results are given in Figure 3, where physical aging is again clearly apparent, consistent with measurements on isotropic molded samples.[3,13–15]

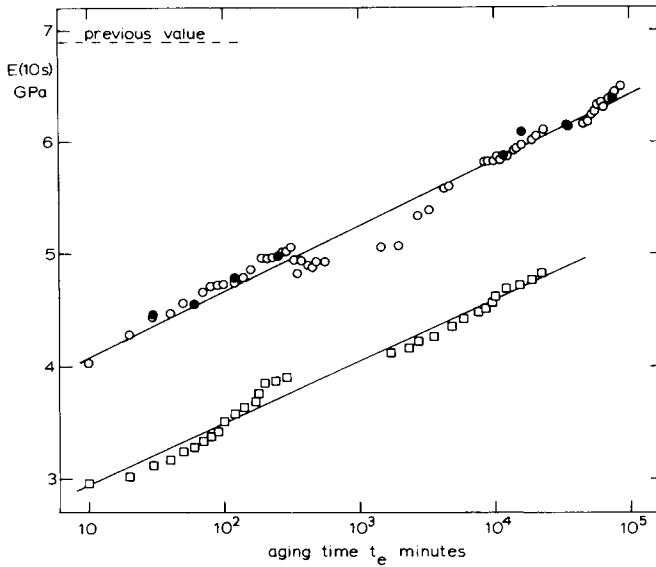If physical aging of drawn PP does not arise through the recrystallization

Fig. 2. Isochronal stress relaxation modulus $E(10\ \mathrm{s})$ vs. t_e during aging of fiber A after heat treatment for 15 s allowing free shrinkage: (O and ●) $T_a = 100°\mathrm{C}$; (□) $T_a = 120°\mathrm{C}$.

mechanism, is it consistent with densification of the noncrystalline fraction, as proposed by Struik[13] (see also Turner[3])? Evidence bearing on this point was obtained from density and melting measurements.

To follow changes in density during aging, short lengths (a few mm) were cut from the heat treated fibers immediately after the quench to 20°C and cleaning of silicone oil and inserted in the density gradient column. Their positions in the column were then monitored over the period of aging and taken to indicate the "apparent density." A control experiment with untreated fiber A showed that a period of 10^3 min was required for a sample to settle at its equilibrium position in the column (Fig. 4). Beyond this point, the apparent density could reliably be assumed to equal the true density. From Figure 4, it is clear that the density of heat-treated samples increases with t_e. That this is not an artefact caused by the effect of column liquids on the fiber is indicated by the relative constancy of apparent density for the untreated sample.
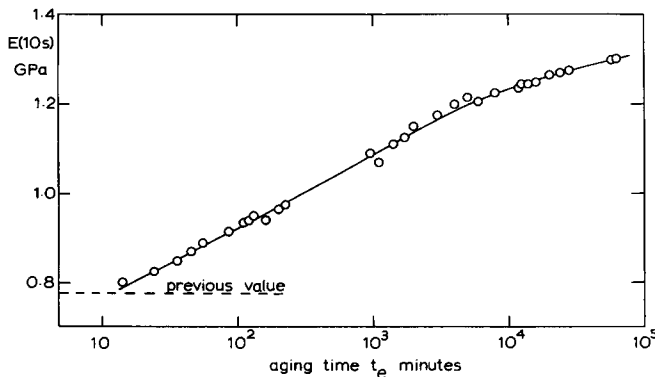

Fig. 3. Isochronal stress relaxation modulus $E(10\ \mathrm{s})$ vs. t_e during aging of fiber B (undrawn PP) after heat treatment for 6 h at 140°C.
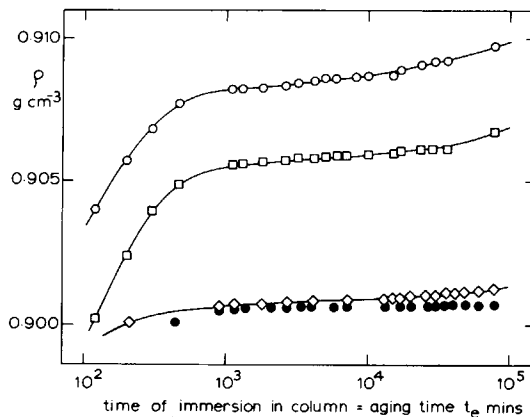
Fig. 4. Apparent density ρ vs. t_e during aging of fiber A after the following heat treatments: (O) 140°C (7 h, CL); (□) 140°C (15 s, CL); (◇) 140°C (15 s, FS); (●) untreated sample. ρ measured by density gradient column at 23°C.

Measurements of ρ, ΔH, and $E(10 \text{ s})$ are brought together in Table I for T_a = 140°C and three combinations of the other parameters of the thermal history (t_a, length constraint, t_e). The striking feature of the data in Table I is the large increase of $E(10 \text{ s})$ with increasing t_e during aging, associated with very small changes in ρ and ΔH. In fact, no changes in ΔH with t_e were resolved above experimental scatter, and the changes in ρ, if interpreted as usual in terms of a crystallinity increase, would indicate an increase of no more than 1.7% (but see below for a more appropriate interpretation of density changes in this case). These variations during aging are in contrast to variations caused by changing other aspects of thermal history. This may be seen in Table I by comparing the

TABLE I
Comparison of Changes in Latent Heat of Fusion ΔH, Density ρ, and Isochronal Stress Relaxation Modulus $E(10 \text{ s})$ During Aging of Fiber A after Three Different Thermal Treatments

T_a, °C	t_a	FS or CL	χ	t_e, min	ΔH, kJ/kg	ρ, g/cm³	$E(10 \text{ s})$, GPa
140	7 h	CL	0.658	65	95.3		3.63
				11×10^2		0.9082	3.90
				15×10^3	97.7	0.9089	5.75
				36×10^3	98.0	0.9093	6.20
				78×10^3		0.9098	7.00
140	15 s	CL	0.627	40	88.9		3.80
				11×10^2		0.9056	3.94
				15×10^3	89.7	0.9060	5.90
				36×10^3	89.9	0.9062	6.40
				78×10^3		0.9068	7.06
140	15 s	FS	0.576	50	93.2		4.20
				11×10^2		0.9008	4.50
				15×10^3	92.8	0.9010	5.65
				36×10^3	93.0	0.9012	6.20
				78×10^3		0.9019	6.70
Untreated sample			0.564		77.5	0.9007	6.90

three heat treatments at constant t_e. Significantly larger changes in ρ and ΔH are associated with much smaller changes in $E(10\,\text{s})$. Table I therefore strongly implies that the physical mechanism of aging is of a quite different nature from that of other heat treatment effects. This gives qualitative support to the model of Struik, especially since densification of amorphous polymers is known to cause large changes in mechanical properties associated with very small changes in density.[2]

To make a more searching comparison, it is necessary to express the model of Struik quantitatively. His proposal[13] is that in a semicrystalline polymer, crystals cause local constraint of noncrystalline molecular segments. This causes a broadening of the glass transition region to temperatures above that where the main effect is observed, for example, the "knee" in volume–temperature plots. Thermodynamic instability of the noncrystalline fraction, observed in wholly amorphous polymers only at temperatures below T_g, therefore extends to temperatures above T_g as normally defined. The course of physical aging following a quench from higher temperatures is then assumed to occur as in wholly amorphous polymers, by a uniform shift of the mechanical relaxation spectrum along the log (relaxation time) axis to longer times, as the excess free volume decays.[13] This proposal is supported by the small-angle X-ray scattering results of Duiser and Keijzers.[22] They showed conclusively that during physical aging of poly(ethylene terephthalate) above T_g, the gradual increase in density results from densification of the noncrystalline fraction.

When the free volume interpretation is applied quantitatively to physical aging of amorphous polymers, it appears to become increasingly inaccurate with decreasing aging temperature below T_g.[13] Here, however, we are concerned with aging *above* T_g, and it is reasonable to assume that segmental mobility *is* determined by free volume through the classical Doolittle equation. The relaxation time shift factor $\ln a$ is therefore given in terms of the fractional free volume f by

$$\ln a(t_e, t_e^*, T) = B\left[\frac{1}{f(t_e, T)} - \frac{1}{f(t_e^*, T)}\right] \tag{1}$$

when referred to a reference aging time t_e^*; B is a constant.

According to this model, an aging experiment on PP proceeds according to the scheme indicated in Figure 5(b), where the specific volume of the noncrystalline fraction v_{nc} is shown. For comparison, aging of an amorphous polymer is indicated in Figure 5(a). The path A–B–C corresponds to quenching (A–B)
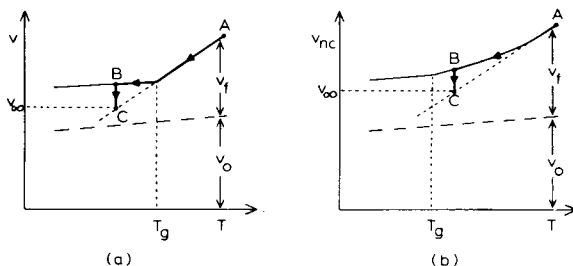

(a) (b)

Fig. 5. Schematic diagram of volume changes during aging of (a) amorphous polymer at $T < T_g$, (b) semicrystalline polymer at $T > T_g$.

and subsequent aging during isothermal storage (B–C). The limiting specific volume (as $t_e \to \infty$) v_∞, free volume v_f, and occupied volume v_0 (all referring to noncrystalline PP) are also shown. Following Ferry,[23] we define f as follows:

$$f(t_e, T) \equiv \frac{v_f(t_e, T)}{v_\infty(T)} = \frac{[v_{nc}(t_e, T) - v_0(T)]}{v_\infty(T)} \tag{2}$$

with a limiting value as $t_e \to \infty$,

$$f_\infty(T) = 1 - \frac{v_0(T)}{v_\infty(T)} \tag{3}$$

which for temperatures T close to T_g would be expected[23] to be close to 0.025. Equation (2) contains a difficulty when applied to a semicrystalline polymer such as PP: v_{nc} is not known. Its limiting value v_∞, however, can be estimated by a variety of means. Here, we choose the value proposed by Natta et al.[24] for amorphous PP at 25°C, 1.18 cm³/g, and denote this approximation by v'_∞, assumed to differ from v_∞ by only a small fraction ϵ'. To circumvent the lack of absolute values of v_{nc} for use in eq. (2), it only remains to take as a reference point a large aging time t_e^*, where v_{nc} can be assumed to differ from v_∞ by another small fraction ϵ. We thus define ϵ and ϵ' through

$$v'_\infty = v_\infty[1 + \epsilon'], \qquad v_{nc}(t_e^*) = v_\infty[1 + \epsilon] \tag{4}$$

(In eqs. (4) and in the following, dependence on aging temperature T is implied.) Changes in v_{nc} can be deduced from the total specific volume v for a sample of mass fraction crystallinity χ through

$$v_{nc}(t_e) - v_{nc}(t_e^*) = \frac{[v(t_e) - v(t_e^*)]}{[1 - \chi]} \tag{5}$$

Combining eqs. (1) to (5) yields

$$\ln a = \frac{-B[1 + \epsilon'][v(t_e) - v(t_e^*)]}{v'_\infty [f_\infty + \epsilon]^2[1 - \chi][1 + \delta_1]} \tag{6}$$

where

$$\delta_1 = \frac{[v(t_e) - v(t_e^*)][1 + \epsilon']}{v'_\infty [f_\infty + \epsilon][1 - \chi]}$$

and is at most ca. 0.2 in the present work. To a first approximation, therefore, we predict $\ln a$ to be proportional to v during aging, through a gradient $-B[1 + \epsilon']/v'_\infty [f_\infty + \epsilon][1 - \chi]$.

It must be recognized, of course, that aging renders χ more difficult to obtain by the density method than is otherwise the case, since v_{nc} is continuously changing. If χ is obtained from specific volume measurements at a time t_e^*, the appropriate expression from volume additivity is

$$\chi = \frac{v_{nc}(t_e^*) - v(t_e^*)}{v_{nc}(t_e^*) - v_c} \tag{7}$$

since the crystal specific volume v_c may be assumed constant. Although $v_{nc}(t_e^*)$ is unknown, we may use eqs. (4) to replace it in eq. (7) by v'_∞, yielding the approximate expression, correct to first order in ϵ' and ϵ,

$$\chi = \frac{[v'_\infty - v(t_e^*)][1 + \delta_2]}{[v'_\infty - v_c]} \tag{8}$$

where

$$\delta_2 = [\epsilon - \epsilon'] \{[v'_\infty - v(t_e^*)]^{-1} - [v'_\infty - v_c]^{-1}\}$$

and is only ca. $5[\epsilon - \epsilon']$ in the present case. In Table I, the values of χ quoted were calculated from eq. (8), assuming $\delta_2 \simeq 0$ and $v_c = 1.059$ cm^3/g,[25] using v measured at $t_e^* = 7.8 \times 10^4$ min.

For two of the specimens referred to in Table I, long-term (10^5 s) tensile stress relaxation tests were carried out, also at $t_e^* = 7.8 \times 10^4$ min; the resulting data are given in Figure 6. If the stress relaxation modulus measured at a time t after loading at an aging time t_e is denoted by $E(t, t_e)$, the assumption of uniform shift of relaxation spectrum during aging can be expressed by

$$E(t, t_e) = E(t/a, t_e^*) \tag{9}$$

Equation (9) was applied to the values of $E(10 \text{ s}, t_e)$ given in Table I and the curves $E(t, t_e^*)$ in Figure 6 to yield $\ln a(t_e)$, which is plotted versus $v(t_e)$ in Figure 7. To within experimental scatter linear relations are obtained, as predicted by eq. (6) in the approximation $\delta_1 \simeq 0$. Furthermore, from eq. (6), together with the approximations $\delta_1 \simeq \epsilon \simeq \epsilon' \simeq 0$ and $B = 1$,[23] the gradients of the straight lines shown in Figure 6 yield values of f_∞ close to 0.025, typical of amorphous polymers
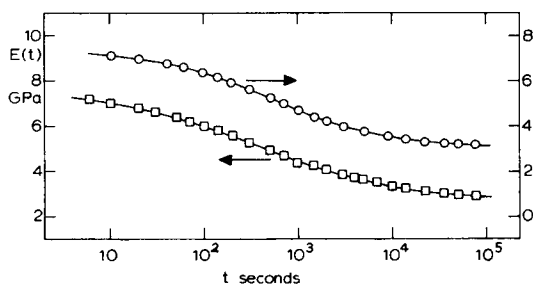

Fig. 6. Stress relaxation curves for samples of fiber A aged for $t_e = 7.8 \times 10^4$ min after heat treatment at 140°C at constant length for the following times: (O) $t_a = 7$ h; (□) $t_a = 15$ s.
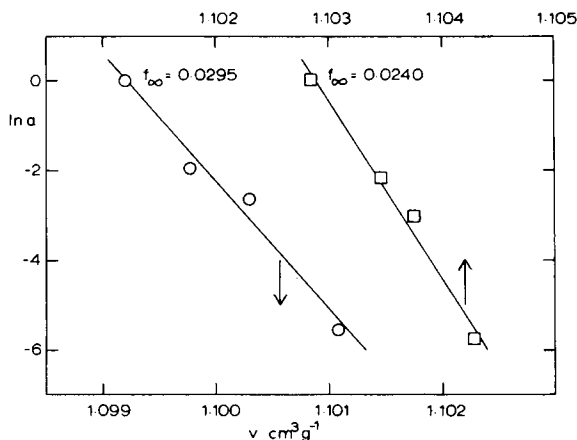

Fig. 7. Shift factor $\ln a$ vs. specific volume v during aging of the two samples of Figure 6 (same symbols). Also given are the values of f_∞ calculated, via eq. (6), from the gradients of the least-squares straight lines shown.

in the glass transition region.[23]   This further supports the mechanism proposed by Struik as applying to drawn fibers of PP.

Notwithstanding this satisfactory consistency with the present data, there is some recent evidence that the proposed model does not accurately describe the situation in PP.   Chai and McCrum[14] have examined carefully the question of whether eq. (9) applies during aging.   They concluded from attempted superposition of creep curves, and from thermally stimulated creep results, that there occurs a distortion of the retardation spectrum during aging.   Slight but systematic changes in shape were observed in creep curves plotted versus log t obtained at different aging times t_e.   Similar effects are discernible in the creep data of Struik.[15]   These cannot be simply interpreted, however, since there will be some aging occurring *during* each creep test, which will distort the measured creep curves in just the sense observed.   No attempt was made in the present work to assess the accuracy of eq. (9) for the present samples.   Its validity to sufficient precision was assumed on the basis of the extensive data of Struik.[13] The quantitative consistency of the model with the present results vindicates this assumption.

Finally, the physical aging discussed here can be identified with a similar effect observed by several authors[26–28] following quenching of PP directly from the melt.   The changes in physical properties observed parallel those found here and elsewhere[3,13–15] after quenches from lower temperatures.   Quenching from the melt results largely in the smectic form of PP.[29]   Now, however, aging can be seen to be independent of the presence of the smectic form.   Fibers A and B used here were studied by wide-angle X-ray diffraction, and visual examination of the diffraction patterns revealed only the stable monoclinic crystal form[25] to be present.

CONCLUSIONS

We have shown that large physical aging effects are observed in drawn fibers of PP, during storage at room temperature after a rapid cool from higher temperatures (even below the melting range).   From our results and those of previous authors, it is clear that such effects are a general property of PP.   Their occurrence does not depend on the presence of a particular crystal form or state of orientation or on the details of the thermal history prior to cooling.   The mechanism proposed by Arridge et al.[12] and Peterlin[21] for a similar phenomenon in highly drawn polyethylene is therefore inapplicable.

The evidence to date points to the cause being the collapse of excess free volume in the noncrystalline fraction.   This has been shown here to extend to a quantitative correlation between changes in stress relaxation modulus and in density.   Why physical aging extends to temperatures above T_g in semicrystalline polymers remains unproven.   A plausible explanation, however, is that due to Struik[13]:   crystals cause a local decrease in segmental mobility of the noncrystalline fraction, thereby broadening the glass transition region.

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