Interaction between viscoelastic and structural relaxation in drawn polypropylene yarn

Y. C. Bhuvanesh and V. B. Gupta*

Textile Technology Department, Indian Institute of Technology, New Delhi 110 016, India
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An unusual observation has been made during stress relaxation experiments on as-drawn polypropylene multifilament yarn which had not been subjected to any conditioning treatment. At 0.5% prestrain and at temperatures of 60°C and above, the stress after an initial decrease registers an increase. This inverse relaxation is not seen for a prestrain of 2% nor for annealed samples. On the basis of the results presented, the occurrence of the inverse relaxation has been attributed to the generation of shrinkage stress, which is a manifestation of structural relaxation during the test and is controlled by the α-relaxation.

(Keywords: polypropylene fibre; stress relaxation; structural relaxation)

INTRODUCTION

It has been pointed out in the literature[1-4] for a number of natural and man-made fibres which are undergoing stress relaxation that if they are allowed to recover a part of the extension initially given to them and then constrained at this new low level of extension, the stress may actually build up with time in the sample rather than decrease. This has been termed 'stress recovery' or 'inverse relaxation' and is believed to be a manifestation of viscoelasticity[3,4], the delayed stress build-up arising from the memory of the sample for its previous thermomechanical history. The present studies on polypropylene yarn have shown stress build-up in the case of the as-drawn sample (with no prior conditioning treatment) during the stress relaxation experiment itself without the need to go to a lower extension. An attempt is made in this article to understand this unusual phenomenon.

It became quite clear in the early stages of the present investigation that the stress increase during stress relaxation was most likely related to the non-equilibrium state of the as-drawn polypropylene yarn. Such a state can result from quenching and is most often observed below the glass transition temperature in amorphous polymers which undergo structural relaxation (for which Struik[5] uses the term physical ageing). Studies[6] on the physical ageing of drawn polypropylene fibres held for several minutes at room temperature, i.e. above the glass transition temperature, showed that free volume collapse in the amorphous phase rather than any form of crystallization was the main consequence of physical ageing, as a result of which there was a stiffening of the structure. Struik[5,7-9] studied the long-term physical ageing of isotropic polypropylene and pro-

posed that the presence of crystallites in polypropylene extended the glass transition temperature to temperatures beyond room temperature, and thus ageing at room temperature could be considered as sub-T_g ageing. Read et al.[10] studied the creep of isotropic polypropylene aged at room temperature for different times and concluded that physical ageing in polypropylene at room temperature is controlled by the α-process rather than the extended glass transition as suggested by Struik. Scherer[11] has recently stated that both types of relaxation relate to the relaxation of the structure; viscoelastic relaxation occurs in the presence of an externally applied stress or strain and structural relaxation when a polymer is cooled from a higher to a lower temperature when the structure first experiences an abrupt contraction and then undergoes gradual rearrangement towards equilibrium. The present studies also suggest that the α-process plays an important role in the stress increase due to structural relaxation during the stress relaxation test.

The investigations reported in this article focus on the time and temperature dependence of stress during the isothermal stress relaxation tests on drawn polypropylene yarns at temperatures of 35, 45, 55, 60, 65 and 70°C. A noteworthy observation from these studies was that while at temperatures from 35 to 55°C conventional stress relaxation behaviour occurs, at temperatures of 60, 65 and 70°C an increase in stress can occur after the stress relaxation test has proceeded for about 15 s or so. To trace the origin of this unusual phenomenon, a number of experiments were conducted which included repeated stress relaxation studies on the same samples over five cycles and three prestrains and thermal shrinkage and shrinkage stress measurements at different temperatures. In addition, some studies were also performed on heat-set samples. Analysis of the results indicated that the as-drawn polypropylene yarn is not in equilibrium and contracts significantly at temperatures

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* To whom correspondence should be addressed

of 60°C and above with a significant contribution being made by the α-process. The contractile stress which is generated can affect the stress relaxation behaviour of the sample, while the shrinkage can affect its creep. The stress relaxation and creep data reduce to normal behaviour when these effects are accounted for.

EXPERIMENTAL

Sample preparation

Multifilament polypropylene fibres were produced from isotactic polypropylene chips (Shell) of melt flow index 23 at a spinning temperature of 260°C and wound at $750 \, m \, min^{-1}$ on a pilot-scale Fourne melt-spinning plant (SST-1207). The spun samples were then drawn on a two-zone laboratory-scale drawing unit at a final take-up speed of $104 \, m \, min^{-1}$. The temperature in the second zone was kept at 130°C and a total draw ratio of 4.33 was obtained. Two additional samples were prepared by annealing the as-drawn yarn in silicone oil at a temperature of 140°C for 5 min in constant-length (taut annealed or TA140) and free-to-shrink (FA140) states.

Measurements

Density and density crystallinity. The density of each sample was measured with the help of a Davenport density gradient column. The liquids used for preparation of the column were isopropanol and diethylene glycol.

The mass fraction density crystallinity (β_d) was estimated from the measured density (ρ) by taking the amorphous (ρ_{am}) and crystalline (ρ_c) densities to be $0.854 \, g \, cm^{-3}$ and $0.946 \, g \, cm^{-3}$, respectively, and using the expression[12]

$$\beta_d = \left(\frac{\rho_c}{\rho}\right)\left(\frac{\rho - \rho_{am}}{\rho_c - \rho_{am}}\right)$$

Optical birefringence. The birefringence of each sample was measured using a polarizing microscope fitted with a tilting compensator.

X-ray diffraction studies. X-ray diffraction studies were carried out to measure crystallinity and crystallite orientation as follows.

(1) To obtain the degree of crystallinity of each sample, two methods were used. The first method was based on the powder technique and was used to estimate the degree of crystallinity (β_x) at room temperature. Since for the as-drawn samples the diffraction peaks were somewhat diffuse, a graphical approach outlined by Natta[13,14] was used for computing β_x. The second method was used for estimating crystallinity at temperatures of 30–150°C in terms of the crystallinity index. The fibre was wound around a sample holder, taking care to ensure that the filaments were parallel. The assembly was mounted in a powder diffractometer fitted to a Rigaku Denki high-temperature attachment which was initially at 30°C. The equatorial reflection was then scanned for 2θ values between 10 and 20° in the step scan mode, each step being 0.01°. The temperature was then raised to the next temperature at $2°C \, min^{-1}$ and held at the test temperature for 2 min, after which the scanning was repeated. The diffraction profile was assumed to be the sum of four Pearson VII peaks (three crystalline peaks corresponding to 110, 040 and 130 reflections and an amorphous peak) and linear background. After deconvoluting, the peak areas could be measured and the crystallinity index calculated by taking the ratio of the crystalline peak areas to the total area.

(2) The Hermans crystallite orientation factor f_c was obtained using the expression[13,14]

$$f_c = \frac{3\langle\cos^2\theta\rangle - 1}{2}$$

where

$$\langle\cos^2\theta\rangle = 1 - 1.099\langle\cos^2\phi_{110,z}\rangle - 0.901\langle\cos^2\phi_{040,z}\rangle$$

In these expressions θ is the angle between the c-axis and the fibre axis (designated as the z-axis) and ϕ the angle between a plane normal and the z-axis. Azimuthal scans at 14.2 and 16.9° for the 110 and 040 reflections were obtained from which $\langle\cos^2\phi_{110,z}\rangle$ and $\langle\cos^2\phi_{040,z}\rangle$ were computed.

Amorphous orientation. The Hermans amorphous orientation factor f_{am} was computed from the measured birefringence (Δn), the degree of crystallinity (β_x) and the crystallite orientation (f_c) using

$$\Delta n = \beta_x f_c \Delta n_c^0 + (1 - \beta_x) f_{am} \Delta n_{am}^0$$

where Δn_c^0 is the intrinsic crystallite birefringence and Δn_{am}^0 the intrinsic amorphous birefringence; they were taken to be 0.0291 and 0.067[13], respectively. Using the measured values of Δn, β_x, f_c and the above expression, f_{am} was estimated.

Boiling water shrinkage. The percentage shrinkage in boiling water (100°C) was obtained by immersing a known length of the yarn (L_0) in boiling water for 5 min and measuring the length after shrinkage (L_s)

$$\text{percentage shrinkage} = \frac{L_0 - L_s}{L_0} \times 100$$

Stress relaxation. The stress relaxation studies were carried out on an Instron tensile tester model 1112. An environmental chamber was used to maintain the multifilament yarn at the required temperature to within an accuracy of about ±1°C. Multifilament yarn, 15 cm long, was clamped between two pairs of jaws, one of which was connected to the load cell. The environmental chamber was taken to the required temperature before mounting the sample between clamps to a known small prestrain (three prestrains were used, viz. 0.5, 1.0 and 2.0%), which was maintained constant in the case of all the samples. The required prestrain was applied at a strain rate of $1.67 \, min^{-1}$ and the stress was measured for 2 h as a function of time elapsed on a chart recorder.

For the repeated stress relaxation test, the sample was removed from the environmental chamber and brought to room temperature. The sample was again used for the next cycle of the stress relaxation test after being left at room temperature for at least 20 h.

Creep. Creep experiments, were carried out on a Stanton Redcroft thermomechanical analyser (t.m.a.) adapted suitably for creep tests. A yarn sample of length

40 mm was mounted inside a cylindrical heating device which could maintain the set temperatures to within $\pm 0.1°C$. The loading arrangement ensured that the load was quickly transferred to the filament. The change in length of the sample under the load was obtained as a function of time on a chart recorder with the help of a very sensitive transducer sensor to which one end of the sample was fixed.

Time dependence of shrinkage. Using the t.m.a., the isothermal time-dependent shrinkage was also obtained in the presence of a very small load to give the sample a slight pretension.

Shrinkage stress. The shrinkage stress was measured by taking a 10 cm long multifilament yarn in the form of a loop and clamping it with a slight pretension on the Instron tensile tester model 1112. A cylindrical heating device which could maintain the set temperature to an accuracy of $\pm 1°C$ was preheated to the required temperature and quickly lowered to surround the sample. As the sample picked up heat, the shrinkage force was sensed by the load cell and recorded as a function of time.

Temperature dependence of shrinkage. The temperature dependence of shrinkage in the as-drawn and annealed samples was obtained with the help of a Perkin–Elmer thermomechanical analyser at a heating rate of $5°C\,min^{-1}$. The data were converted to show the percentage shrinkage as a function of temperature.

RESULTS AND DISCUSSION

Structural data

The structural data for the as-drawn and the two annealed fibres are presented in *Table 1*. The as-drawn sample is seen to be a well-oriented, semicrystalline fibre with a significant amount of residual stress, which gives rise to high shrinkage. On heat-setting, crystallinity increases while amorphous orientation decreases, the decrease being particularly significant in the free-annealed sample. The shrinkage of the annealed samples is much lower than that of the as-drawn sample, indicating that on annealing residual stresses may have relaxed to a significant degree.

Data on the as-drawn sample

Stress relaxation data. Detailed stress relaxation studies were performed on the as-drawn sample under isothermal conditions for 2 h at selected temperatures

Table 1 Some structural data on as-drawn and heat-set polypropylene fibres

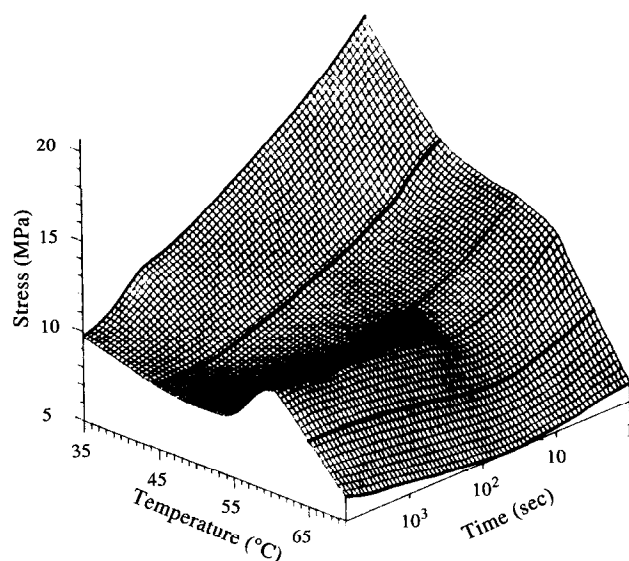|	As-drawn fibre	Heat-set fibres	
		TA140	FA140
Density ($g\,cm^{-3}$)	0.907	0.912	0.913
Birefringence	0.039	0.043	0.038
Crystallinity (%) (density)	60.1	65.4	66.5
(X-ray)	52.5	59.8	61.4
Crystallite orientation f_c	0.942	0.974	0.87
Amorphous orientation f_{am}	0.82	0.65	0.38
Boiling water shrinkage (%)	8.5	3.4	0.4

Figure 1 A three-dimensional representation of the time-dependent stress relaxation curves of the as-drawn polypropylene sample at various temperatures for a prestrain of 0.5%
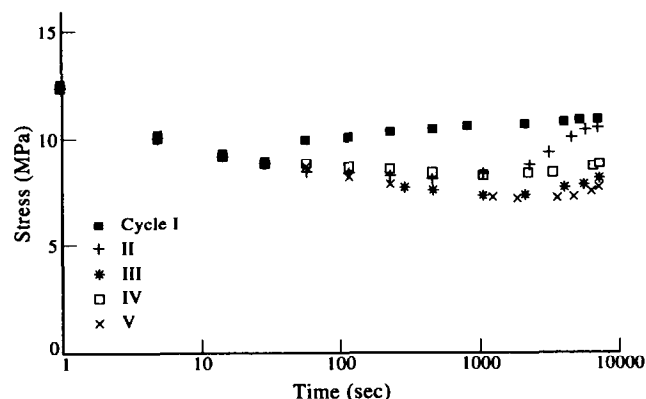

Figure 2 The stress relaxation curves of the as-drawn polypropylene sample at a temperature of 60°C for a prestrain of 0.5% over five repeated tests

between 35 and 70°C at prestrains of 0.5, 1 and 2%. The results for a prestrain of 0.5% are shown as a three-dimensional plot in *Figure 1*. The three-dimensional plot was obtained by using Surfer graphics software which creates a surface grid of equidistant lines by carrying out interpolations in between the data points; the experimental lines are highlighted in the figure. It is immediately obvious that the as-drawn yarn shows unusual stress relaxation behaviour. As expected, relatively high stresses are generated at low temperatures and short times. The stress–time curves at temperatures up to 55°C show the expected fall in stress with increasing time. Around 60°C and above some unusual behaviour is observed. The stress after an initial fall during the stress relaxation test begins to increase (reverse relaxation). The intensity of the stress reversal is maximal at 60°C. A noteworthy observation from *Figure 1* may be made at this stage by closely examining the stress–temperature isochronals, viz. that the rate at which the stress decreases shows a transition around 60°C, which coincides with the onset of the α-transition.
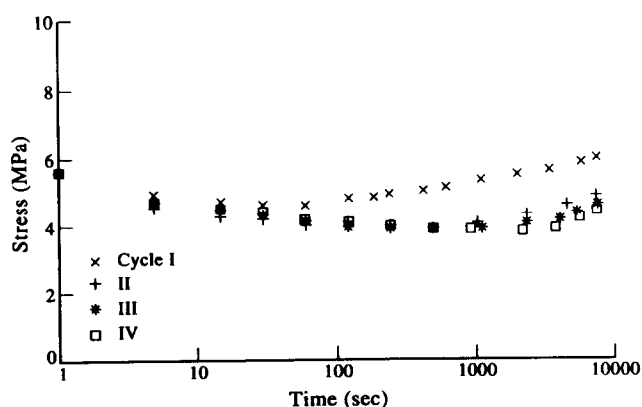
Figure 3 The stress relaxation curves of as-drawn polypropylene fibres over four repeated tests at a temperature of 70°C for a prestrain of 0.5%
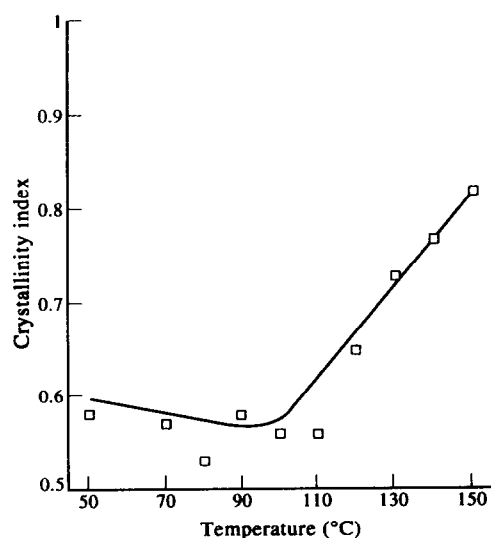

Figure 5 Time-dependent development of shrinkage stress at various temperatures for the as-drawn sample

Figure 4 Temperature/dependence of the crystallinity index for the as-drawn sample

Figure 6 Time dependence of the percentage shrinkage at various temperatures for the as-drawn sample

Figure 7 Experimental stress relaxation curves at 60°C (O) and 70°C (●), shrinkage stress curves at 60°C (□) and 70°C (■), and corrected stress relaxation curves at 60°C (△) and 70°C (▲) for the as-drawn sample

The relaxation of stress with time, according to Scherer[11], is a composite response arising from both viscoelastic and structural relaxation. The most likely reason for the observation of the structural relaxation would be the non-equilibrium nature of the as-drawn sample. Hence repeated stress relaxation tests on the same sample were carried out under identical conditions of prestrain (0.5%) and temperature (60°C). The data are shown in *Figure 2* and two features are noteworthy: firstly, the intensity of the reverse relaxation reduces with each successive test; and secondly the time at which reverse relaxation occurs is shifted to longer times, e.g. the time at which reverse relaxation occurs shifts from 10 s in the first cycle to about 500 s in the fifth cycle. Similar broad features can be observed even at 70°C also, as shown in *Figure 3*.

These observations clearly indicate that significant irreversible changes are occurring in the as-drawn fibres during the stress relaxation tests performed at 60°C and above. The shifting of the location and the reduction of the intensity of the reverse relaxation phenomenon are both manifestations of an approach towards equilibrium. This could arise either as a result of secondary crystallization or owing to free volume collapse, i.e.
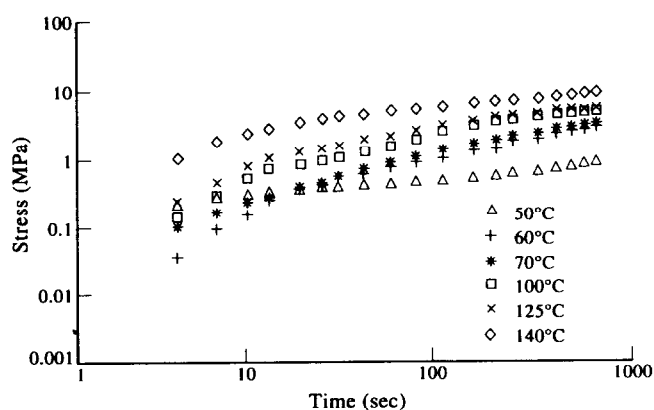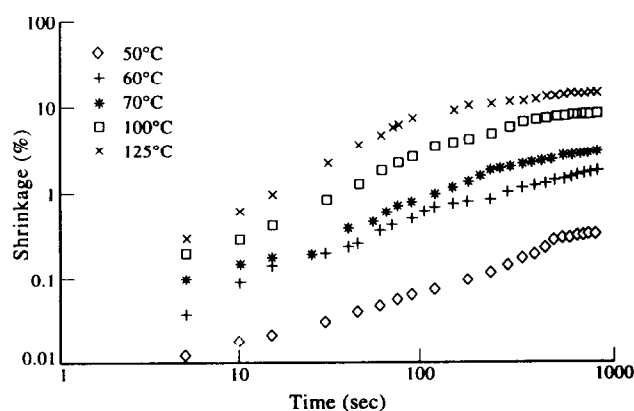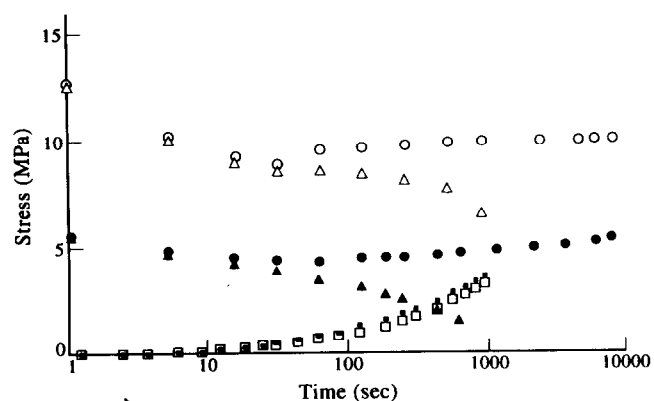
physical ageing. Measurement of the crystallinity index showed that there is no change in crystallinity at temperatures right up to 100°C, as shown in *Figure 4*. The density of the sample was found to increase from 0.907 g cm⁻³ before the test to 0.9075 g cm⁻³ at the end of the fifth cycle. Thus it appears that densification of the amorphous phase occurs during the repeated stress relaxation tests.

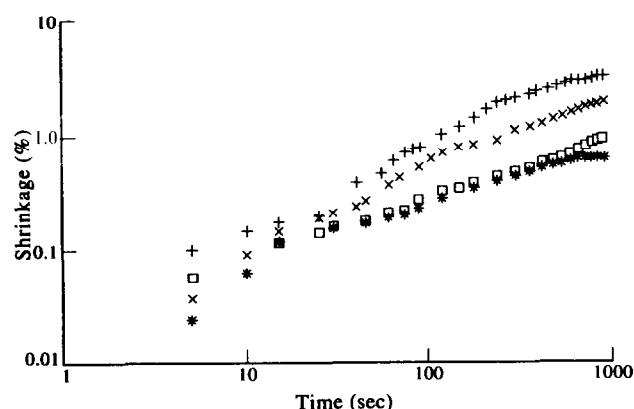It has been pointed out by Trznadel[15] that the major

Figure 8 Free shrinkage of the as-drawn sample at 60°C (×) and 70°C (+), after five cycles of stress relaxation at 60°C (∗) and after four cycles of stress relaxation at 70°C (□)
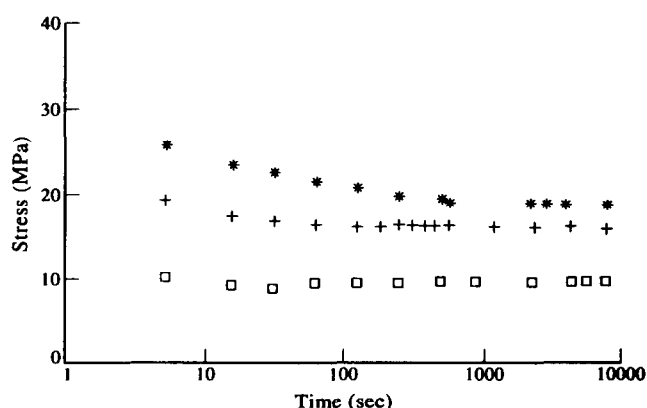

Figure 9 Stress relaxation curves at 60°C for prestrains of 0.5% (□), 1% (+) and 2% (∗) for the as-drawn sample
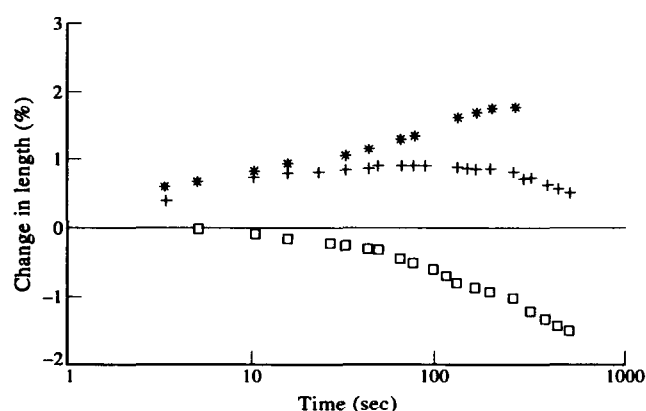

Figure 10 Experimental creep curve (+), free shrinkage curve (□) and corrected creep curve (∗) at a temperature of 60°C for the as-drawn sample

Figure 11 Comparison of the stress relaxation curves for as-drawn (■), free-annealed (+) and taut-annealed (∗) samples obtained at a temperature of 60°C for a prestrain of 0.5%

Figure 12 Percentage shrinkage as a function of temperature for as-drawn (□), taut-annealed (+) and free-annealed (∗) samples at a heating rate of 10°C min⁻¹

effect of ageing is confined to the gradual relaxation of initial stresses 'frozen in' after deformation. It was therefore of obvious interest to make measurements of the shrinkage stress and shrinkage for the present samples.

Shrinkage behaviour. The shrinkage stress data for the as-drawn sample are shown in *Figure 5*, while the shrinkage behaviour is shown in *Figure 6*. The shrinkage stress develops gradually but it does not show any tendency to
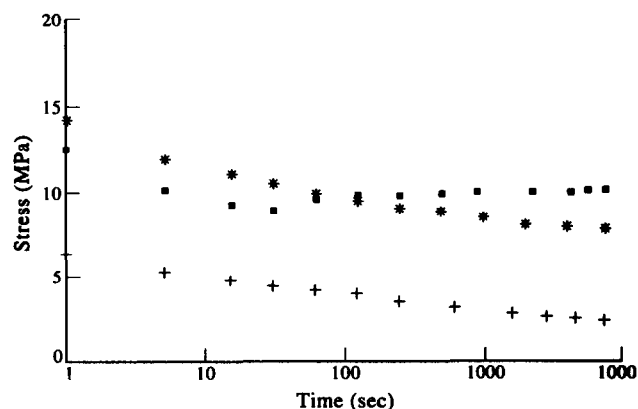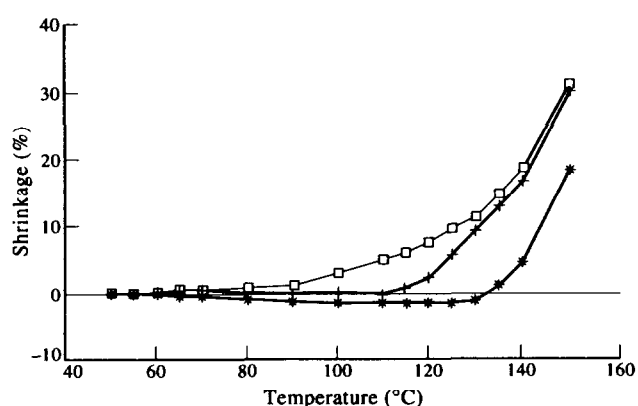
relax. The development of shrinkage also proceeds gradually.

The next obvious step was to attempt to differentiate and exclude the structural relaxation effect from the composite effect of viscoelastic and structural relaxation in the stress relaxation data presented earlier so that only the viscoelastic effect dominated the stress relaxation curves. As shown in *Figure 7*, when the stress generated through structural relaxation is removed from the composite curve, the unusual stress increase during the stress relaxation test is no longer present. Samples obtained after being subjected to repeated stress relaxation tests for five cycles at 60°C and for four cycles at 70°C were tested for the time dependence of the shrinkage behaviour. The data obtained are shown in *Figure 8*, and it can be clearly seen that the samples subjected to repeated cycles of stress relaxation show less shrinkage, indicating that the sample is gradually moving towards equilibrium.

In order to obtain further insight into the origin of the inverse relaxation phenomenon, the stress relaxation experiments were carried out at 60°C with higher start-up prestrains of 1 and 2%. The data are shown in *Figure 9*. It is noteworthy that at 1% prestrain reverse relaxation is less intense than at 0.5%, while at 2% prestrain the reverse relaxation phenomenon is almost absent. This is apparently because at the higher prestrains the magnitude of the stress build-up is higher

and the contribution from structural relaxation is not very significant.

Creep data. From a creep experiment carried out under a relatively low load of 5.3 MPa and at a temperature of 60°C, it was observed that after the initial increase in length as expected there was a decrease in length as shown in *Figure 10*. This unusual effect complements the observation of reverse relaxation or stress build-up during stress relaxation. It would be expected that the residual stresses will try to relax during the creep experiment and the resultant shrinkage would be superimposed on the creep. As shown in *Figure 10*, the composite creep curve reduces to a normal creep curve when account is taken of the contribution of shrinkage.

Data on annealed samples

The stress relaxation curves for the two annealed samples are shown in *Figure 11*; the data for the as-drawn sample are also included for reference. It is observed that both the annealed samples, viz. TA140, and FA140, do not show any reverse relaxation. Since the structure would be expected to come close to the equilibrium state when heat treated at the high temperature of 140°C, any possibility of major structural reorganization during the stress relaxation test at a temperature around 60°C will be very limited. This is further borne out by the data on the boiling water shrinkage (*Table 1*) of the annealed samples. The data obtained from thermomechanical analysis, presented in *Figure 12*, indicate that the shrinkage begins to take place only at temperatures above 110°C in sample TA140; the α-relaxation will be expected to play an important role in this. In the as-drawn sample the onset of shrinkage is at a temperature of around 60°C, which is also the temperature of onset of the α-transition. In the FA140 sample, there is a small extension before the sample shrinks at a temperature of around 125°C. The extension during the initial stage of the experiment is not surprising considering that the sample has undergone substantial randomization during the annealing treatment. Thus the observed shrinkage would also include the small lengthening of the sample up to around 125°C. The total shrinkage at the end of the experiment in both the annealed samples is much smaller than in the case of the as-drawn sample. The residual stresses are very high in the as-drawn sample compared to those in the annealed samples.

CONCLUSIONS

Unusual behaviour is shown by as-drawn polypropylene fibres undergoing stress relaxation at temperatures of 60°C and above and at a prestrain of 0.5%. It is observed that the stress after an initial relaxation begins to increase. This build-up in stress has been attributed to the non-equilibrium nature of the as-drawn sample resulting from the presence of high residual stresses. The origin of this effect has been discussed. It has been shown that unlike the reverse relaxation effect reported in the literature, which is a manifestation of the viscoelasticity of the polymeric fibre, the stress reversal observed in the present studies is due to structural relaxation.

ACKNOWLEDGEMENT

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