Retraction of polypropylene tape†

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Retraction measurements have been made on 50 μm thick polypropylene tapes drawn on a yarn line under a variety of conditions. Small samples were annealed in silicone oil for different periods at temperatures up to the melting point. The retraction data were found to be described by a relation of the form $R(\%)=A+B\log t$, where A and B are constant for a given temperature, A being the intercept on the retraction axis for $t=1$. As the temperature is increased towards the melting point, A increases, slowly at first and then much more rapidly. On the other hand, B reaches a maximum at a temperature T_k, and then decreases as the temperature is increased further. T_k corresponds to the point at which A, which represents a virtually instantaneous retraction as the sample reaches temperature, begins to increase rapidly. T_k promises to be useful in that it represents the susceptibility of a given polymer to retraction and corresponds fairly closely to the original draw temperature if the tape has not been heat set. D.s.c. analysis has demonstrated that the mechanism responsible for the instantaneous component of retraction is the partial melting out of crystallites. The small logarithmic retraction which is dominant below T_k is seen as resulting from a thermally activated process within the crystallites. The approach has enabled the effect of pre-anneals and heating rates to be understood and has also led to a general prediction of retraction behaviour under conditions of continuous heating.

INTRODUCTION

The tendency of drawn crystalline polymers to shrink when heated to temperatures below the melting point is described as retraction. This is of particular industrial significance. It can effectively limit the scope of subsequent processing at elevated temperature e.g. dyeing and cause problems in service. Oriented polypropylene films, tapes and fibres are notably liable to retraction. It is generally considered necessary to control the effect by subjecting the drawn polymer to a heat-setting process, in which it is reheated in the region of its melting point while the retraction is mechanically limited to a small but controlled amount. The importance of retraction measurements in characterizing drawn polymer products is indicated by the fact that they are covered by a British Standard specification (for polypropylene yarns this is BS4611: 1976).

Retraction (or thermal shrinkage) is not confined to drawn crystalline polymers. An amorphous glassy polymer can be formed at elevated temperatures when in the rubber state, and the shape can be frozen in by cooling through the glass transition. It is not surprising that on reheating into the T_g region, the material will retract to its original shape, the driving force for the change being the entropic character of the molecular network. There is general agreement that, for drawn crystalline polymers, the driving force for retraction is similarly entropic, and this view is supported by the results reported here. However, there are important differences between variously published experimental facts and a significant divergence of theories proposed in explanation. The objective of this work has been to study in detail the retraction of drawn polypropylene homopolymer in the form of tape, in order to explain existing anomalies in the literature and draw together salient aspects of current theories.

SCIENTIFIC CONTEXT

Materials previously studied

Most previous work has been carried out on polymers which have crystallized from oriented melts, i.e. yarns, tapes, films and injection mouldings[1–3,4,8] although there are significant papers based on material which has been drawn in the solid state[6,7,9].

In broad terms, reported retraction behaviour is similar for polymers variously processed, and such differences which are apparent cannot be correlated with either polymer type or processing route.

Retraction behaviour

In one of the earliest detailed studies of retraction, Keskkula and Schmitt[8] working with injection moulded polypropylene found that the retraction reached an equilibrium value within 2 min when held at constant elevated temperature. If the temperature was raised closer to the melting point, the retraction rapidly increased to a higher equilibrium value. The retraction observed was temperature dependent. Most subsequent observations have supported these basic findings. However, Hansen, Kracke and Falender[6,7] demonstrate that, for cold drawn polyethylene and polypropylene, the retraction continues to increase gradually with log time after the first rapid contraction, whereas Baltá-Calleja and Peterlin[9] working mainly with cold-drawn polypropylene state that retraction remains constant after the initial effect at all except the lowest temperature.

The importance of the heat transfer medium used in the retraction experiment was shown by Dumbleton[1] who obtained greater retractions for anneals in silicone oil than in air. In re-examining Dumbleton's data, Samuels[3]

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Table 1

Code	Draw ratio	Draw temperature	Annealing treatment
7/160/–	7 : 1	160°C	–
7/115/–	7 : 1	115°C	–
7/115/A	7 : 1	115°C	30 min silicone oil 100°C
7/115/HS	7 : 1	115°C	Heat set on line 225°C
5.5/150/–	5.5 : 1	160°C	–

suggested that the difference was due to the different heat transfer efficiencies. This explanation is also in accord with the observations of Asano[2] and Keskkula and Schmitt[8] that a low temperature pre-anneal reduces the amount of retraction observed.

Concurrent with retraction, there is generally a decrease in modulus[1,4], an increase in long period as measured by small angle X-ray diffraction (SAXD)[1,9], an increase in the intensity of the first small angle diffraction maximum[1,9] and an increase in density[4,9].

One of the simplest models proposed to explain retraction was that of Keskkula and Schmitt. They suggested[8] that retraction was the result of the melting out of crystallites smaller than a given size. Such a model is attractive in that it accounts for the rapid attainment of retraction equilibrium for a particular temperature. It also provides a qualitative explanation of pre-annealing effects in terms of the perfection, growth and, hence, increase in the melting point of some of the crystallites. However, it does not account for the observations of a continuing but gradual increase in retraction at longer times[6,7]. Several subsequent theories are more complicated and envisage additional processes such as chain-refolding[1], thickening of crystalline layers[2], and the crystallite shear approach of Peterson[5]. In the Peterson model, crystallites sheared by the drawing process are seen as reverting to their original shape by chain slip mechanisms, with the potential reduction in fold surface area and, hence, energy as the driving force. The model is not really applicable to structures crystallized from oriented melts in which there is probably little shear deformation present. Peterson viewed his mechanisms as supplementary and did not propose them as a replacement for existing models. However, Falender and Hansen[7] interpret their data as supporting the model.

Retractive force measurements

In this type of experiment the specimen is heated at constant length and the development of retractive force measured. Hansen *et al.*[6] carried out their experiments at successively higher temperatures and observed the development of an equilibrium force at each. On the other hand, recent papers by Arridge, Barham and Keller[10] and Barham and Arridge[12] describe an experiment in which the retractive force is measured as the temperature is gradually raised. For polyethylene, the force decreased gradually with temperature until 120°C, where there is an irreversible increase followed by a plateau (with a gradual increase proportional to T) and then a second large increase just prior to melting. They explained their results using a detailed composite model. The experiment is essentially different to the free retraction one, and has not formed part of the current programme; however, the possible relevance of some of our d.s.c. measurements on clamped specimens to this work means that it will be discussed again later.

EXPERIMENTAL

Materials used

For this study we used 34 mm wide, 50 μm thick polypropylene tapes produced from extruded sheet by ICI on a commercial line. The draw temperatures, nominal draw ratios and annealing treatments are summarized in *Table* 1 along with the codes used to refer to them in this paper.

Definition of retraction

In accord with previous workers we define % retraction as:

$$\%\ \text{retraction} = \frac{L_d - L}{L_d - L_0} \times 100$$

where L_d = drawn length;
L_0 = undrawn length;
L = length after retraction.

Retraction measurement

For most of the retraction experiments, the specimens were heated in silicone oil in a thermostatically controlled bath at constant temperature ± 0.01°C. We also used air and boiling water anneals to illustrate the dependence of the % retraction on the annealing medium.

For both the oil and water experiments, the specimens were suspended on a loop of thin wire and immersed directly in the liquid. This simple suspension system had the advantage of minimizing the local temperature drop of the liquid on immersion, which may be quite large for more elaborate rigs[9]. For the retraction experiments in air, the heating time was reduced by immersing the specimens in pre-heated alumina sand.

Heat flow computations have been made in order to estimate how quickly the tape attains the temperature of the oil bath. The assumption was made that the temperature of the oil was not reduced by the immersion of the tape. For an initial tape temperature of 20°C and with oil at 150°C, it was estimated that the tape reaches within 5°C of the final temperature in ~0.5 s, within 1°C by ~0.75 s and within 0.1°C by ~1 s. Thus, the tapes would have been well within the vicinity of the annealing temperature for the times at which the retraction data were recorded.

At the end of the retraction experiments, all the specimens were quenched in water at room temperature before measurement of L. L_0 was determined by measuring the length of the specimen after a short anneal in silicone oil above the melting point of the polymer, when complete retraction is obtained without the specimen flowing in any viscous sense. The tapes with a nominal draw ratio of 7:1 were observed to retract to a length 1/25th that of the drawn tape. We explain the difference by the orientation present in the extruded polypropylene which, in the undrawn state, can produce shrinkage to just under 1/3 the original length.

L_0, L_d and L were determined by measuring the distance between two crosses, one at each end of the specimen,

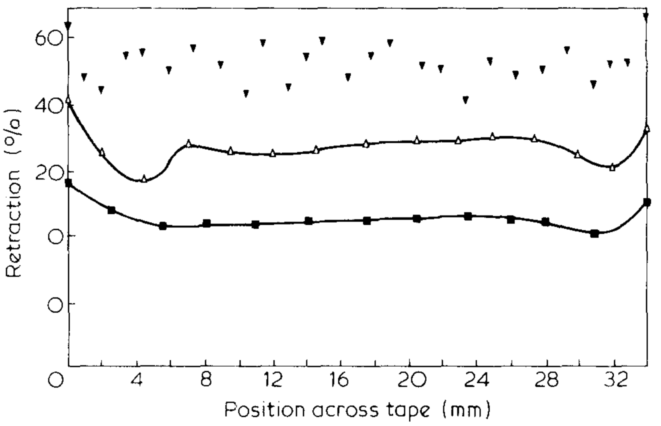


Figure 1 Variation in the percentage retraction obtained across the width of the tape for 7/160/–. Annealed for 1 min at 150°C in silicone oil: ■, whole: △, in stripe 2.5 mm wide; ▼, in strips 1 mm wide; ■ and △ are displaced downwards by 20%

using a micrometer on the stage of a projection microscope.

Uniformity of tape

Initial experiments showed considerable variation in the % retraction obtained across the width of the tape (*Figure* 1). The magnitude of the retraction after 1 min at 150°C depended on whether lengths of the tape were heated as supplied or in the form of narrow strips. Whereas both the tape heated as supplied and that in 2.5 mm wide strips displayed approximately constant retraction in the central section of the tape with marked edge effects, the tape in very narrow 1 mm strips showed marked variation in the measured retraction across the entire width. These experiments indicated that we should not use the edges of the tape and also determined the minimum width necessary to obtain consistent and representative results.

We also observed a small variation in retraction along the length of the tape. As it is desirable for all the specimens to be identical when comparing results in one set of experiments (e.g. all annealed at one temperature for various times), they were all cut from the same section of tape and made as small as practically possible (bearing in mind that errors in measurement increase with a decrease in length). 15 mm × 3 mm was chosen as an optimum size and only the central half of the tape was used so as to avoid edge effects.

RESULTS

As all the tapes showed a similar dependence of the % retraction on the temperature and time of the experiments in silicone oil, we shall describe the general behaviour first and then compare the results for tapes with different processing histories.

At all temperatures, there is an initial extremely rapid increase in retraction which is followed by a much more gradual increase (*Figure* 2). When plotted as a graph of % retraction *versus* log time the data points lie on straight lines for each temperature (*Figure* 3). On the graph, each value plotted corresponds to the mean of nine experimental values. At temperatures at which comparison was possible, we could detect no difference between the retraction behaviour of specimens in oil or water. However, treatment in air led to lower values of retraction. Unfortunately retraction measurements made using silicone oil at high temperatures for long times were complicated by an apparent swelling of the specimens which eventually disintegrated. This behaviour was apparently due to absorption of the oil[11] and we do not base any of our analysis on data from long time immersions at high temperatures.

ANALYSIS

Variation with time

The log time dependence of retraction can be formalized in the relation:

$$R = A + B \log t$$

where $R = \%$ retraction;
t = time within the range 2 s to 100 h.

A and B are constant with respect to R and t but depend strongly on the annealing temperature. Baltá-Calleja and Peterlin have used equations of this type to fit experimen-

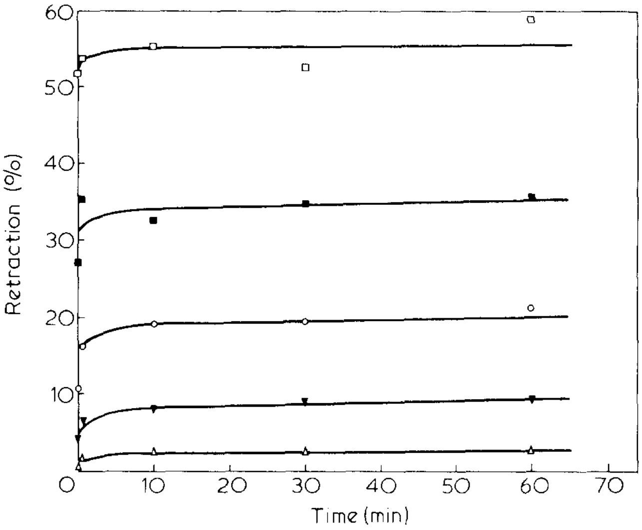


Figure 2 Retraction of 7/160/– in silicone oil as a function of time and temperature. □, 150°C; ■, 145°C; ○, 140°C; ▼, 130°C; △, 100°C

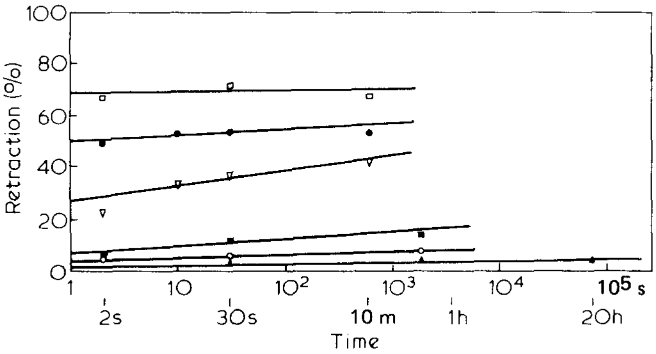


Figure 3 Retraction of 5.5/160/– in silicone oil as a function of time and temperature. □, 155°C; ●, 152.5°C; ▽, 150°C; ■, 145°C; ○, 140°C; ▲, 120°C

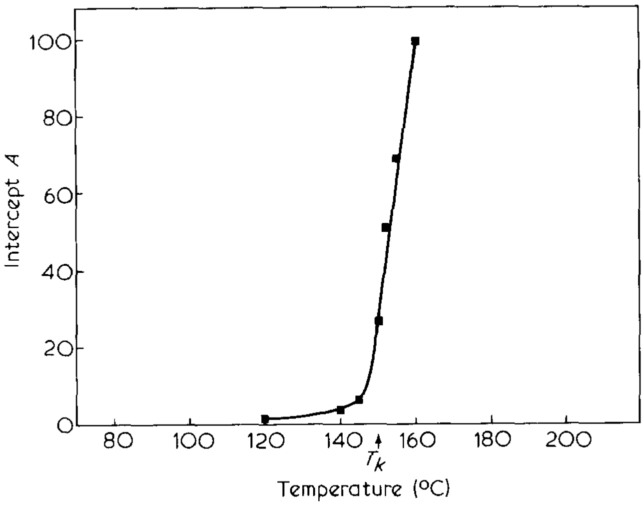


Figure 4 Variation of the parameter *A* with temperature for 5.5/160/–

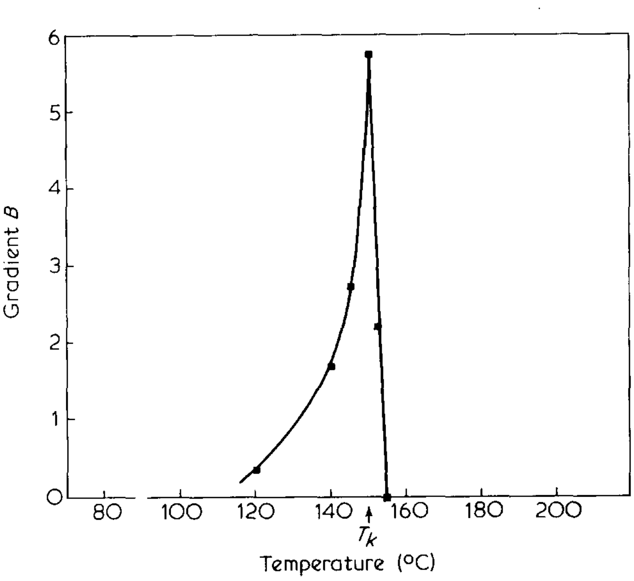


Figure 5 Variation of the parameter *B* with temperature for 5.5/160/–

tal data for long periods measured by SAXD, the intensity of the meridional maximum of SAXD and density in shrinkage experiments.

Since the time taken for the tapes to attain the annealing temperature is of the order of 1 s (i.e. $\log t = 0$), the constants A and B can be viewed with the following significance. A can be considered to represent the instantaneous retraction on reaching the annealing temperature, whereas B is a measure of the magnitude of the continuing time dependent retraction.

Variation with temperature

The variation of retraction with temperature is best illustrated by observing the dependence on temperature of A and B in the equation $R = A + B \log t$. Examples are shown for 5.5/160/- (*Figures* 4 and 5). For this sample, and in fact for all tapes examined, A increases more rapidly with temperature as the melting point is approached, whereas B shows a pronounced maximum at a temperature below the melting point which we refer to as T_k. Comparison of the curves will show that it is in the region of T_k that the values of A begin to increase rapidly. (T_k is indicated on the plots of both A *versus* T, and B *versus* T).

Comparison for different tapes

All the tapes showed an increase in retraction with time as log time. For each tape we present graphs of A and B *versus* temperature (*Figures* 6 and 7). The peak temperature, T_k, in the B *versus* T plot (*Figure* 7) increases with draw temperature and appears to have a value within 20°C of this temperature. Of the two samples drawn at the same temperature but to different draw ratios, i.e. 5.5/160/- and 7/160/-, the higher draw ratio corresponds to the lower T_k. In addition, the drastic effect of heat setting in raising T_k is apparent from comparison of curves 7/115/HS and 7/115/-.

If specimens are pre-annealed just below the retraction temperature, the total retraction obtained is reduced. The effects of pre-annealing for different times and temperatures are illustrated in *Figures* 8 and 9. It is apparent that these results correlate with the observations that the total retraction obtained above T_k is reduced if the specimen is brought to temperature relatively slowly, as is the case for treatment in 'air' (*Figure* 10). Pre-annealing increases T_k (c.f. curves 7/115/A, and 7/115/- of *Figure* 7).

Comparison with previous work

The results of our experiments are at variance with those of several workers, in that they show that retraction increases gradually with log time after the initial rapid contraction. The data of Hansen, Kracke and Falender[6] for polypropylene also show the gradual increase with log time, and we have fitted these to the empirical relation $R = A + B \log t$. Again, a maximum is apparent in the plot B *versus* T but it is in the region of 60°C, which is still below the corresponding temperatures for our specimens (*Figure* 11). We relate this difference to the fact that their specimens were 'cold' drawn at 40°C, whereas ours were recrystallized from stretched melts above 100°C.

The corresponding results of Baltá-Calleja and Peterlin

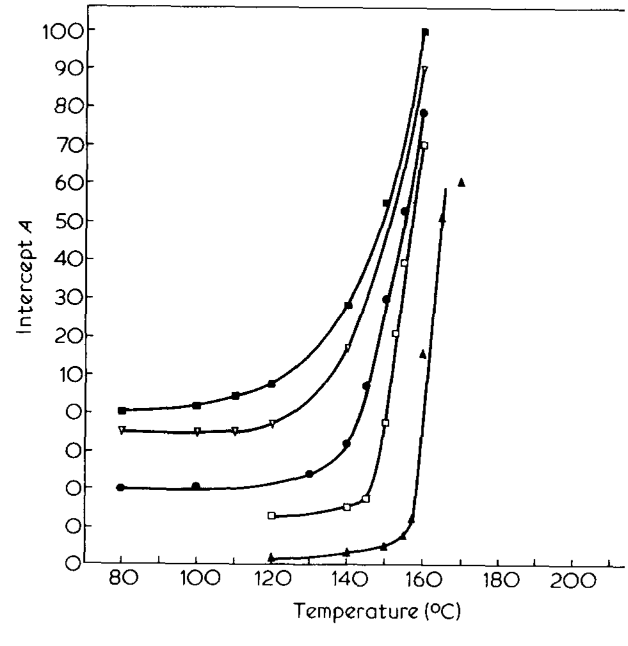


Figure 6 Variation of the parameter *A* with temperature for all the tapes. ■, 7/115/–; ▽, 7/115/A; ●, 7/160/–; □, 5.5/160/–; ▲, 7/115/HS. Curves ▽ to ▲ are offset vertically in increments of 10 units to avoid confusion

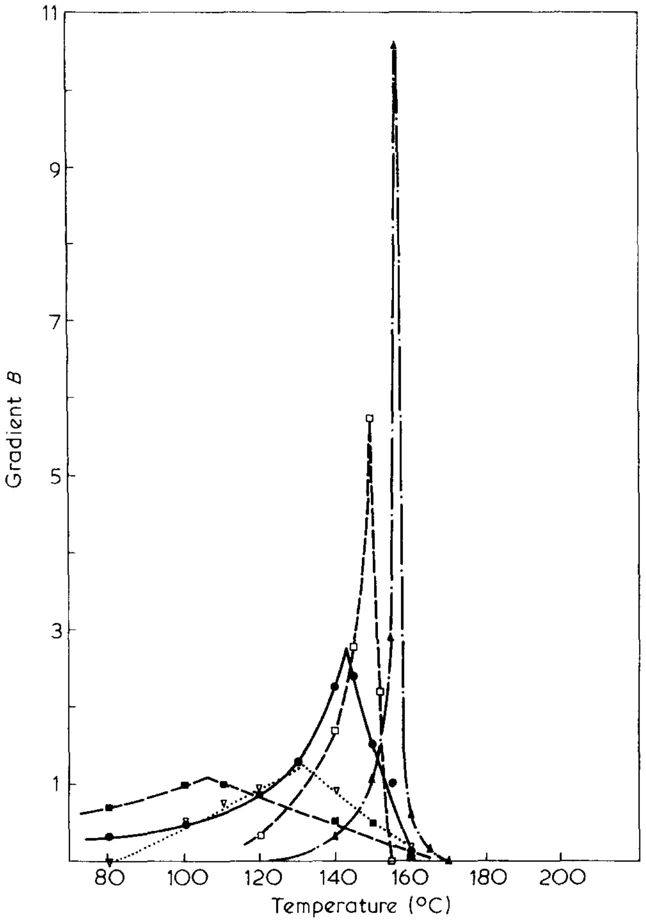


Figure 7 Variation of the parameter B with temperature for all the tapes. ■, 7/115/–; ▽, 7/115/A; ●, 7/160/–; □, 5.5/160/–; ▲, 7/115/HS

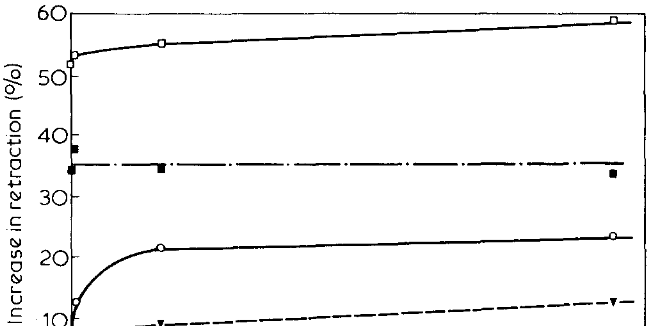


Figure 8 Graphs showing increase in retraction as a function of time of treatment at 150°C in silicone oil for specimens which had been pre-annealed at 140°C for the times indicated. The pre-anneals in silicone oil which produced the retractions indicated in brackets were for the following times. □, No pre-anneal; ■, 2 s (11% retraction); ○, 10 min (19% retraction); ▼, 1 h (21% retraction)

also appear to show a similar trend, although the authors do not draw attention to this. This is somewhat surprising, as they use the $A+B \log t$ relation to analyse their measurements of SAXD long period, SAXD first peak intensity and density. The variation in the constant B with temperature for their data is also plotted in *Figure* 11. Again, there is a maximum in B, in this case at approximately 60°C for the cold drawn specimens (20°C).

Therefore, it appears that there is a broad correlation between T_k and draw temperature over a range wider than that covered by our experiments. *Figure* 12 demonstrates the correlation.

Differential scanning calorimetry

A model for retraction involving melting out of the crystalline regions appears attractive in that it can account for the almost instantaneous initial retraction above T_k. In such a model partial melting out is seen to allow a degree of relaxation of the molecular chains which are pinned in their stretched conformation by the crystals through which they pass. The driving force for retraction

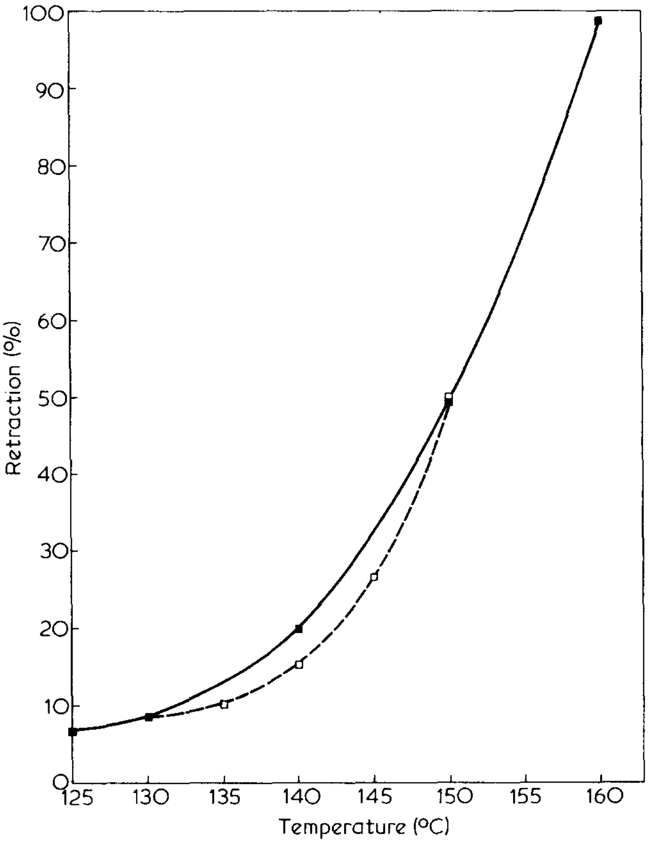


Figure 9 Effect of pre-annealing on the total retraction obtained in silicone oil for 7/160/–. ■, Heated for 10 min at each temperature. □, Pre-annealed for 10 min at 130°C before heating at each specific temperature for 10 min

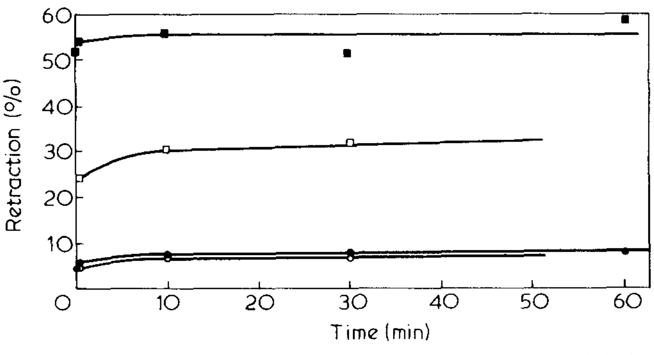


Figure 10 Effect of annealing medium on the retraction of 7/160/– as a function of time at two temperatures. Annealing media and temperature: ■, silicone oil at 150°C; □, air at 150°C; ●, silicone oil at 130°C; ○, air at 130°C

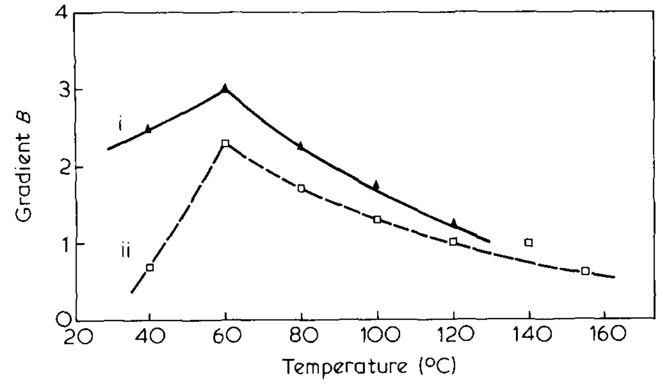


Figure 11 Variation of the parameter *B* with temperature replotted from published data: ▲, Hansen, Kracke and Falender[6]; and □, Baltá-Calleja and Peterlin[9]

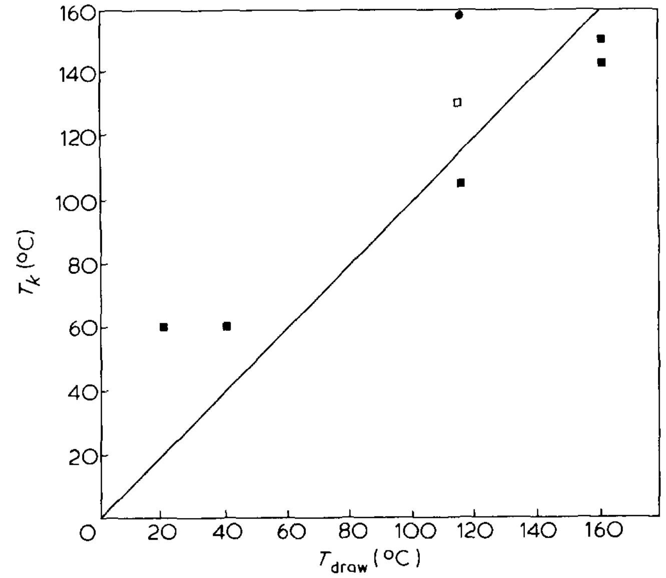


Figure 12 Correlation between T_k and T_{draw} (□ pre-annealed, ● heat set)

is the increase in entropy and decrease in internal energy obtained on shrinkage as in the amorphous polymer, that is the contraction of the stretched 'rubber network'. In an effort to test this model, we observed partial melting-out of the crystallites using differential scanning calorimetry (d.s.c.).

The machine used was a Perkin Elmer DSC II at a scan rate of 80°C min^{-1}. Appropriate calibration was made and corrections for thermal lag applied. Traces were obtained both from specimens which were allowed to retract in the cell and from specimens which were clamped so as to prevent retraction. Retraction of a specimen during a d.s.c. run can lead to spurious data as the quality of thermal contact between specimen and pan varies. We attempted to obviate this difficulty by chopping the specimen into very fine pieces (< 1 mm^3) with a razor blade prior to placing in a lightly crimped pan. For runs in which retraction was to be prevented, the sample was very firmly held between a heavily crimped pan and lid. In general, the unclamped material exhibited a rather broad endothermic peak whereas the clamped specimens produced either double peaks or a peak with a pronounced shoulder. Examples are shown in *Figure* 13. The double peak is probably the result of melting and recrystallization occurring during the d.s.c. scan; this has been proposed previously for poly(ethylene terephthalate)[13]. D.s.c. runs with unclamped specimens correspond to the free retraction experiments which form the basis of this work, and it is the peaks from these runs which will be considered in detail.

The presupposition that the area under the endothermic melting peak up to a particular temperature can be taken as a measure of the amount of material that has melted out up to that temperature, and hence the retraction possible, has been tested in *Figure* 14 by plotting percentage instantaneous retraction at tempera-

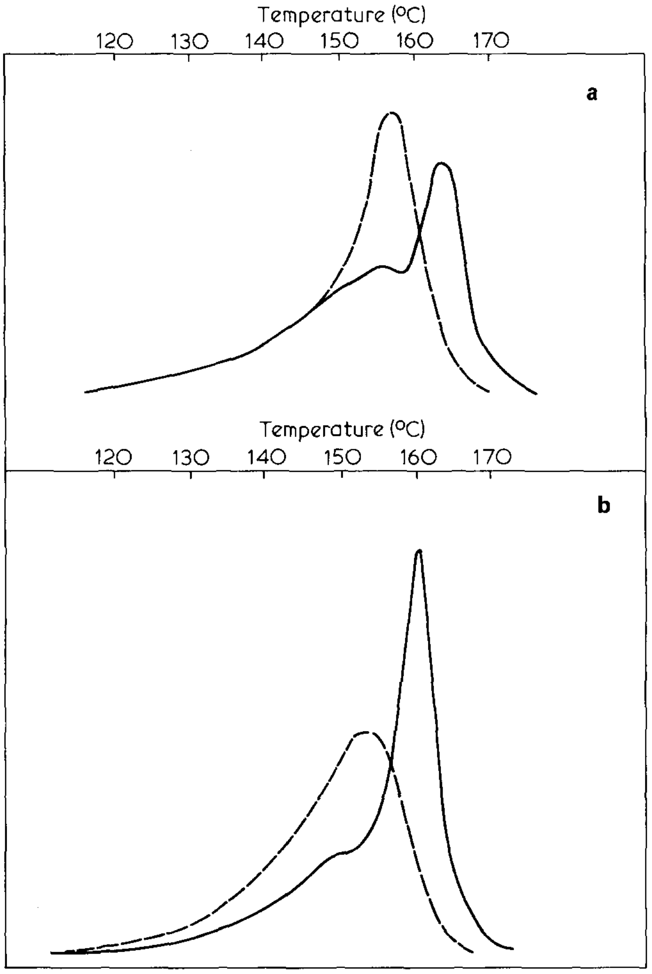


Figure 13 DSC traces of: (a) 7/115/HS; (b) 7/115/–. ——, Clamped specimen, – – – –, unclamped specimen

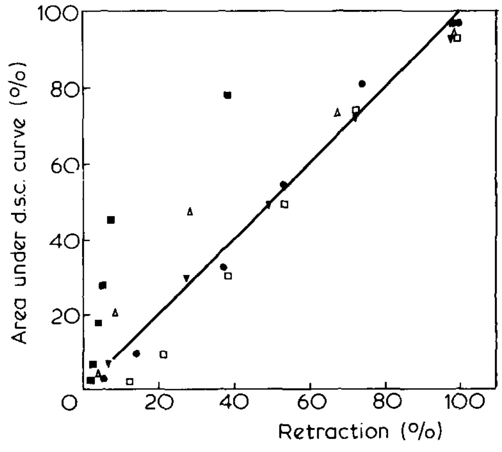


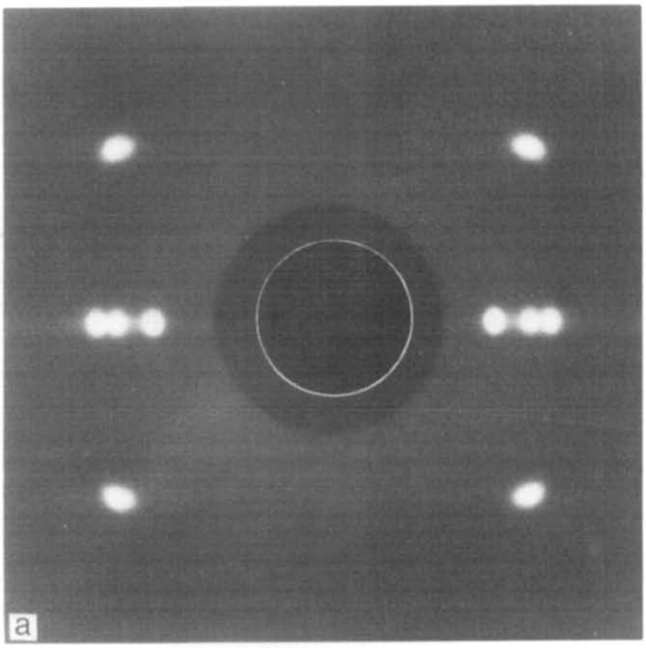
Figure 14 Correlation between the fraction of crystalline material melted out and the instantaneous retraction for all the tapes: □, 7/115/–; ●, 7/115/A; ■, 7/115/HS; ▲, 7/160/–; △, 5.5/160/–

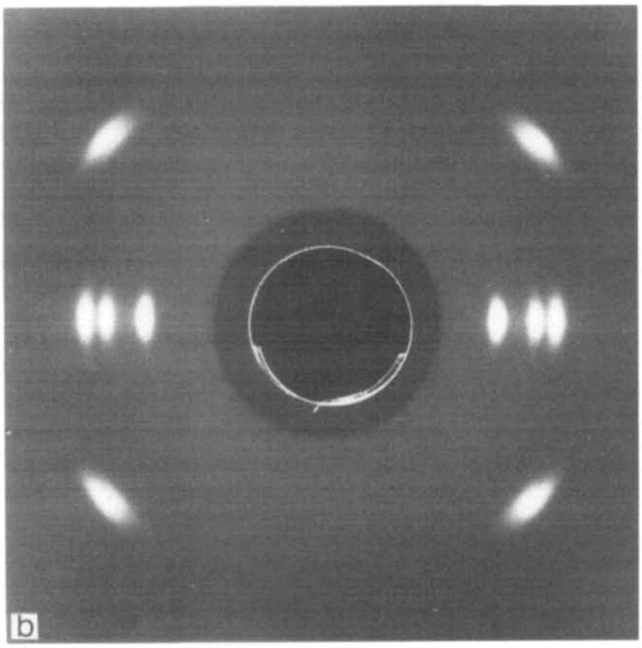
ture T against the percentage of the endotherm area below T. For all the tapes except 7/115/HS (the heat set one), there is excellent correlation between the amount of material melted out and the instantaneous retraction at all temperatures.

DISCUSSION

Instantaneous component of retraction

The retraction which occurs immediately the specimen is brought to temperature, measured by the parameter A (e.g. *Figure* 4), only becomes significant above a particular temperature, which we refer to as T_k. The lack of any time dependence of this component of retraction supports the view that it is the consequence of partial melting of the specimens. A proportion of the crystallites, which pin the molecular network in its highly extended conformation, melt, thus permitting the partial relaxation of the network and hence retraction.





The recrystallization of the melted-out material is expected to occur, but at these elevated temperatures it will require significantly longer than is necessary for the immediate retraction.

The correlation between retraction and area under the d.s.c. melting endotherm for unclamped specimens integrated up to the retraction temperature (*Figure* 14) provides strong evidence in support of the melting-out model. It also suggests a rapid method by which the retraction of a drawn (but not heat set) polymer may be estimated for different temperatures from a single d.s.c. trace. The melting endotherm is derived primarily from latent heat. However, in situations in which retraction occurs, there may be an additional contribution due to the increase in entropy at constant internal energy of the rubbery network itself; but it will only be present if the retracting sample is able to do work. Also, it is not thought to be significant as the total area under the d.s.c. melting peak for samples which are clamped to prevent retraction is very similar to that for free samples (although the shapes are different); and furthermore, even if it did make a substantial contribution to the endotherm, its direct relationship to percentage retraction would ensure that it would not affect the % retraction/% area correlation.

Further evidence for melting-out above T_k can be seen in the WAXD patterns of the polypropylene tapes in *Figure* 15. *Figure* 15*b* is the pattern for specimens 7/160/- after 10 min at 145°C, while *Figure* 15*c* is the pattern after 30 s at 155°C. As well as greater loss in orientation, the bottom photograph shows evidence of '*a*' texture, which is due to a fraction of the material having recrystallized epitaxially with the *a* axis parallel to the *c* axis of the substrate, a rotation of about 80°. The '*a*' texture is apparent as maxima on the first diffraction ring (110) in the region of the meridian.

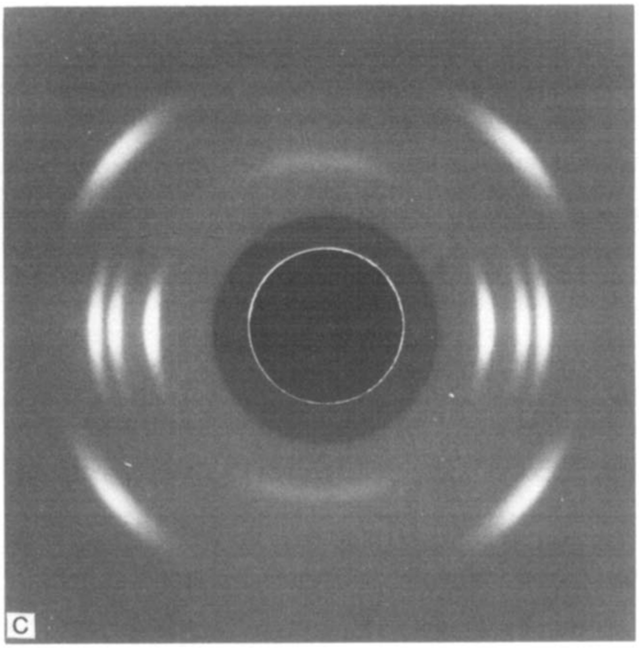


Figure 15 Wide-angle X-ray photographs of 7/160/—: (a) as received; (b) after 10 min heat treatment at 145°C; (c) after 30 s heat treatment at 155°C

The d.s.c. scans were made at $+80°C\ min^{-1}$, under which conditions the entire melting sequence is completed in less than 15 s. The fact that recrystallization is unlikely to occur in this period with the temperature high and rising appears to be confirmed by the observation that the endotherms are single peaks.

The temperature T_k, at which the instantaneous retraction becomes significant, appears to be related closely to the processing history. For the yarn line material which was the subject of this study, the values of T_k showed some correspondence with nominal draw temperatures. However, when data of Hansen, Kracke and Falender[6] and Baltá-Calleja and Peterlin[9] are included, the T_k/T_{draw} correlation can be seen over a much wider temperature range (*Figure* 12). If we take into account that the high draw temperatures, which refer to on-line oven temperatures, are likely to be over-estimates, and that the two 'cold-draw' temperatures are possibly underestimates, owing to heating of the samples by the drawing process, then the correlation is improved. Therefore, it appears that for the high draw temperatures, the temperature at which melting out, and hence instantaneous retraction, first occurs is close to the temperature at which the crystallites formed. The equivalent correspondence for the 'cold-drawn' samples, between initial melting out and previous draw temperature, appears to provide additional support for Peterlin's model of cold drawing based on the mechanisms of transient melting in response to a combination of heat of deformation and a reduction in T_m due to tensile hydrostatic stress localized in the necks of microfilaments[14].

Logarithmic component of retraction

This component is present over the complete temperature range of the retraction phenomenon. Its contribution increases with temperature to a maximum at T_k and then decays as the instantaneous component becomes dominant.

We propose that the logarithmic component below T_k is due to the gradual reduction in the effectiveness of the crystallites as locks to hold the molecular network in the extended conformation. The logarithmic time dependence suggests a mechanism involving creep of the crystallites, and the rapidly accelerating magnitude of the parameter B (slope of the retraction *versus* log t plot) indicates that the process is thermally activated.

The rapid increase in the logarithmic component with temperature is terminated abruptly at T_k. The onset of melting out of a proportion of crystallites appears to lead to a reduction in the creep rate of those remaining. There are three possible reasons for such behaviour:

(a) the instantaneous retraction of the network due to melting out would reduce the driving force for creep of the crystallites which remain. On the other hand the reduction in the number of network locking crystallites would tend to increase the stress which each has to bear. So it is difficult to see how these two factors, in combination, can account for the drastic reduction in logarithmic retraction above T_k;

(b) the crystallites which melt out first, being the less perfect, are those which probably contribute most to the logarithmic (creep) component. Thus, the remaining fraction of crystals is more creep resistant as the temperature increases, an effect which will be enhanced if their perfection is further increased by annealing mechanisms which are independent of those which produce creep;

(c) during constant temperature retraction experiments, the melted out fraction will subsequently recrystallize at the retraction temperature, and thus make an additional contribution to the locking of the network. Even though it is likely that the new crystals will grow in the unstressed state, any additional creep of the unmelted crystallites will rapidly lead to a transfer of some of the network stress to the freshly formed ones.

Effect of pre-annealing and heat setting

The data in *Figure* 8 shows the effect of pre-anneals at 140°C, which is below T_k (145°C for 7/160/-), on subsequent retraction at 150°C. The pre-anneal has the effect of decreasing not only the subsequent retraction, but also the total retraction obtained. The reduction in retraction at 150°C is due entirely to a decrease of the instantaneous component (A) and in fact the magnitude of the pre log factor B increases with increasing pre-anneal time. The pre-annealing increases T_k, which suggests that it is perfecting at least some of the crystallites and raising their melting temperature.

Figure 9 shows the result of pre-annealing further below T_k. The total retraction in the temperature range up to 20°C above the pre-anneal temperature is decreased by a small amount, the main effect being a decrease in the logarithmic constant B. This apparent discrepancy with the results for the 140°C pre-anneal can be resolved on examination of the A *versus* T and B *versus* T plots in *Figures* 6 and 7 for the samples 7/115/A and 7/115/- (which were both drawn at 7:1 at 115°C, but 7/115/A had been subjected to a pre-anneal for 30 min at 100°C). Comparison of the two A *versus* T plots shows that the pre-anneal has delayed the onset of the rapid rise with temperature of the instantaneous retraction (i.e. T_k), an effect which is accompanied by the shift of the peak in the B *versus* T plot to a higher temperature. However, up to at least 108°C (T_k for the unannealed sample), the pre-anneal reduces the magnitude of b. The effects of a pre-anneal are two-fold:

(a) to decrease the magnitude of logarithmic retraction;

(b) to delay to a higher temperature the onset of instantaneous retraction and hence increase T_k.

The increase in T_k means that the marked supression of the logarithmic component as the instantaneous component becomes significant is also correspondingly delayed to a higher temperature; so that in the temperature range immediately below the T_k for the pre-annealed sample, the logarithmic component is effectively increased by the pre-anneal.

The marked effect of a pre-anneal in reducing the magnitude of subsequent retraction is seen as the explanation of the influence of heating medium on retraction illustrated in *Figure* 10. Specimens such as those treated in air which are brought to temperature relatively slowly have, in effect, been subject to a series of pre-anneals before the designated temperature is reached.

Comparison of the A *versus* T and B *versus* T curves (*Figures* 6 and 7) for samples 7/115/- and 7/115/HS shows that as far as we are able to detect the effect of heat setting is equivalent to pre-annealing, in that T_k is increased.

One other aspect of the data on the heat set sample is that, in this case, the 1:1 correlation between retraction and d.s.c. peak area was not present (*Figure* 14). The d.s.c. melting peak appears to begin to develop at temperatures

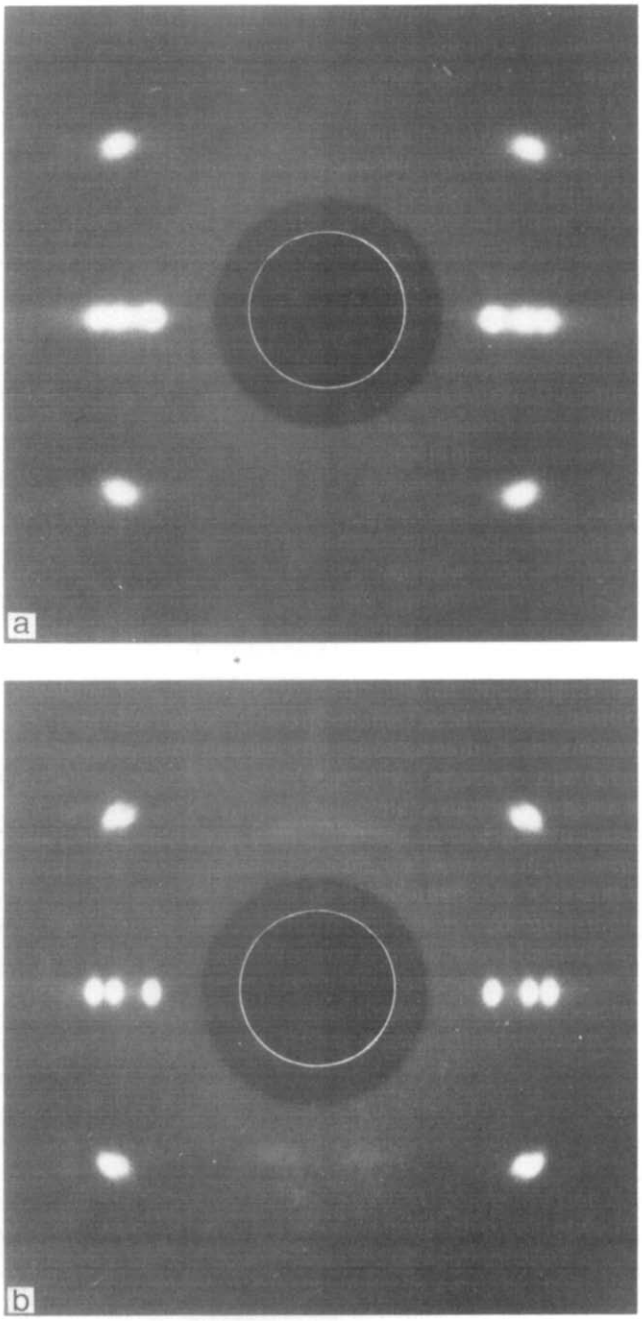


Figure 16 Wide-angle X-ray photographs: (a) 7/115/– as received; (b) 7/115/HS as received

below which there is any significant retraction. We suggest that a clue to this disparate behaviour is given in the WAXD pattern of the heat set sample (*Figure* 16*b*) which shows the development of some '*a*' textured material. It has been shown that the '*a*' component of drawn polypropylene melts first[15], but, because the molecular axis of this component is at about 80° to the draw axis, it is difficult to see how its melting can contribute to retraction. In this way, it is possible to account for an initial increase in the d.s.c. endotherm which is not accompanied by a corresponding retraction.

The tape 5.5/160/- also shows the presence of some '*a*' textured material in the WAXD pattern of the as-received material, and it is noteworthy that in this case also the correlation between the retraction and area under the d.s.c. peak is not as good as that shown by the other tapes.

Melting endotherms of clamped specimens

Figure 13 shows two examples of a general distinction between d.s.c. melting endotherms of specimens which are free to retract and those which are clamped. The free specimens generally show a single melting peak which correlates well with measured retraction. The clamped specimens, however, tend to show two peaks. The first is at approximately the same temperature as the single peak for the corresponding unclamped specimen. We interpret this (in accord with [13]) in terms of an initial melting of some crystallites followed by a temperature range in which further melting is accompanied by recrystallization, which reduces the height of the endotherm, which is subsequently followed by a final complete melting. The reason why recrystallization during heating, the source of the double peak, only occurs for clamped specimens is that the recrystallization rate will be much higher if the specimen is held extended. This phenomenon, which is familiar for natural rubber, has both thermodynamic and kinetic origins. The melting point of crystals in a molecular network which is held stretched is increased, because the entropy of melting is reduced due to the lower entropy of the stretched melt; and the pre-alignment of the molecules in the stretched network can conceivably enhance the rate at which they can be organized in crystals.

The observation of the correspondence between double peaks and clamped specimens qualitatively explains the retractive force measurements of Arridge, Barham and Keller[10] made as a function of continuously increasing temperature (which were outlined above). The initial increase in force appears to correspond to the first d.s.c. peak, the plateau region to the temperature range in which melting and crystallization occur at the same time, and the second increment of force to the final melting out phase.

CONCLUSIONS

(1) The retraction behaviour of polypropylene tape can be resolved into two components. One component of the retraction occurs immediately the specimen reaches temperature, the other develops gradually with time.

(2) Retraction at any temperature follows the law: $R(\%) = A + B \log T$

(3) For any particular sample of tape there is a temperature T_k below which the instantaneous retraction (related to A) is insignificant but above which it increases rapidly. T_k corresponds to a maximum in the logarithmic component of retraction (B).

(4) T_k is related to the thermal history of the polymer. It corresponds closely to the draw temperature except where there has been a post-draw anneal or heat setting treatment, in which case T_k is increased.

(5) The instantaneous component of retraction at a particular temperature is directly related to the area, up to that temperature, under the melting endotherm of a d.s.c. trace of an unclamped specimen. However, this direct proportionality is lost if the specimens have been heat treated such that there is evidence for *a–c* texture in the X-ray fibre patterns.

(6) A model is proposed which accounts for the instantaneous component of retraction in terms of melting out of a fraction of the crystallites which lock the

molecular network in the extended conformation, and the logarithmic component in terms of the creep of the crystallites.

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