JOURNAL OF MATERIALS SCIENCE **34** (1999) 2065–2073

The morphology of woven polypropylene tapes compacted at temperatures above and below optimum

J. TECKOE, R. H. OLLEY, D. C. BASSETT*
J. J. Thomson Physical Laboratory, Whiteknights, University of Reading, Reading RG6 6AF, UK

P. J. HINE, I. M. WARD
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK

The morphology of woven polypropylene cloth compactions, prepared at a series of temperatures, has been examined by electron microscopy following permanganic etching. With increasing temperature, the interior structure of the fibres is seen to undergo progressively greater melting and recrystallization in the form of shish-kebab structures while the volume of melt surrounding the fibres increases. The regions of recrystallized extra-fibrillar melt show effects of flow-induced orientation in the form of row structures. The presence of boundaries persisting where recrystallization fronts have met is interpreted as an effect of segregation of low molecular weight material. © *1999 Kluwer Academic Publishers*

1. Introduction

A number of recent papers [1–4] have described the process of hot compaction whereby individual high modulus thermoplastic fibres, notably polyethylene [1, 2], may be processed to form thick section, continuous sheets retaining comparable properties to the original fibres. Initial studies [3] on polypropylene focused, as in polyethylene, on the use of unidirectionally aligned fibres; however this process necessitated the use of an open mould and, for this polymer, produced inadequately compacted samples even at a compaction temperature of 174 °C, the highest possible with this arrangement. In the current study woven polypropylene tapes have been used with a closed mould arrangement which has allowed compaction temperatures as high as 190 °C. A previous paper [4] compared the mechanical and thermal properties of sheets compacted over a range of isothermal compaction temperatures and related these to the differing degrees of consolidation. In this paper the internal structure and morphology of compacted polypropylene tapes have been examined for processing temperatures above and below the optimum (182 °C) to reveal more of the nature of the crystallization and annealing processes involved in the compaction process.

2. Experimental

The materials and compaction procedures are the same as those described previously [4] using individual isotactic polypropylene tapes of the order of 200 μm wide and 25 μm thick. The fibres were woven with a nominally plain weave (style 1863), with each tow composed of between 10 and 15 tapes. Compacted sheets 2 mm thick were manufactured in a 7 inch (178 mm) square mould using a hot press. Stacked layers of woven cloth were cut and placed in the mould and heated to the desired compaction temperature under a holding pressure of 2.8 MPa (400 psi). Once at temperature the assembly was held for a further 10 minutes, after which a higher pressure of 7 MPa (1000 psi) was applied for 10 seconds before cooling at a nominal 3 K min^{-1} to 100 °C under this pressure. The assembly was then removed from the press and allowed to cool to room temperature. Samples were compacted using this procedure at temperatures ranging from 166 to 190 °C.

Prior to electron microscopy, tape composite specimens were cut perpendicular to their long axis using a glass knife on a cryomicrotome at a temperature of −70 °C. This exposes both longitudinal and transverse sections of differently oriented tapes which could be examined as prepared or, more usually, after permanganic etching for 1 hour in a 1% solution of potassium permanganate in a 10 : 4 : 1 (by volume) mixture of concentrated sulphuric acid and orthophosphoric acid (85%) and water, [2, 5]. In some cases the surfaces were examined using scanning electron microscopy (SEM) after gold coating, otherwise standard two-stage replicas were produced for transmission electron microscopy (TEM).

The thermal properties of certain samples compacted at 168, 172, 182 and 190 °C, were compared by

---

* Author to whom all correspondence should be addressed.

0022–2461

differential scanning calorimetry using a Perkin Elmer DSC-2 operating at 10 K min^{-1}.

3. Results and discussion

In the compaction process polymer tapes are held and annealed under constraint at temperatures above the melting point of the unoriented polymer. As the temperature is raised progressively the oriented tapes begin to melt and the molten material starts to fill the space between tapes in the original structure. At too low a compaction temperature there is insufficient molten polymer to fill all gaps but when this condition is attained then properties are optimal. At still higher compaction temperatures more polymer melts than is required and, since this recrystallizes as normal chain-folded lamellae, the overall properties of the composite decline from their peak. The morphologies of the original tape structure and of compactions at the optimum temperature have been described previously [4, 6]. The present paper describes and discusses the morphologies produced at compaction temperatures above and below the optimum leading to a fuller understanding of the compaction process.

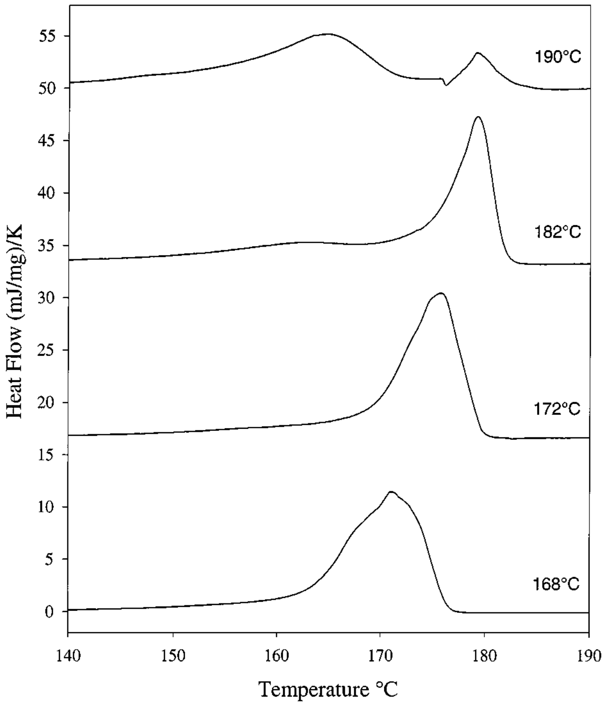


Figure 1 DSC melting endotherms of samples compacted at 168, 172, 182 and 190 °C.

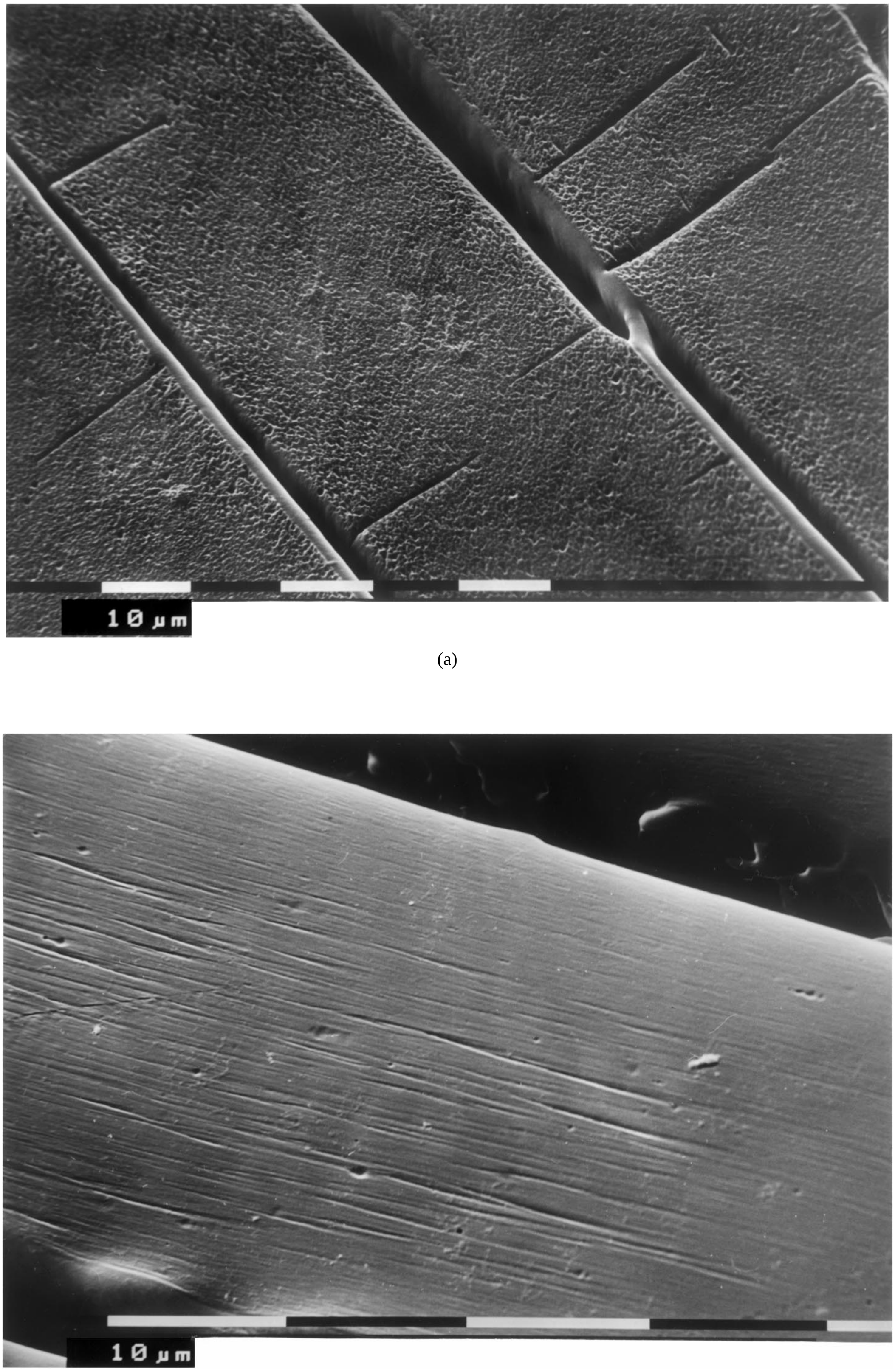
3.1. DSC analysis

The thermal properties of the compactions can be seen in Fig. 1, where with increasing compaction temperatures two peaks can be observed to develop. The lower temperature peak can be seen at compaction temperatures of 182 and 190 °C, with the relative sizes of the two peaks varying significantly with increased compaction temperature. The lower temperature peak is due to recrystallized material and increases at the expense of the higher temperature peak as compaction temperature rises. This is clearly a consequence of increased melting and recrystallization throughout the sample.

3.2. Uncompacted cloth

Fig. 2 shows the woven uncompacted cloth, unetched. When this material is embedded, etched and cut the tapes are seen in both longitudinal and transverse section. A higher magnification view of a transverse section can be seen in Fig. 3a. This shows three individual

Figure 2 SEM micrograph of the original woven polypropylene fabric.



(a)

(b)

Figure 3 (a) SEM micrograph of an etched transverse section of three polypropylene tapes. Note the cracks running perpendicular to the tape axis and the pitted nature of the surfaces. (b) SEM micrograph of an etched longitudinal section of polypropylene tape. Note the grooves running along the tape axis and the highly aligned fibrillar structure.

tapes in one bundle whose etched surfaces are pitted and contain small cracks running part way across. In the present case it is likely that the cracks have been accentuated chemically by the etchant, and are a consequence of bending forces experienced by the tape during manufacture. The small pits observed across the surface are typical of highly drawn material and are a consequence of regions of high free volume (reduced density), which have been preferentially removed by the etching process. These regions are observed as etched out grooves parallel to $\underline{c}$ in longitudinal section, as can be seen in Fig. 3b.

3.3. General features

Fig. 4 reveals an overall perspective of a sample compacted at 184 °C, with the front face (F) displaying the woven construction of the compacted block; this surface was exposed by cryo-microtomy, then etched; this is representative of the sample's internal structure (the material along the left edge is carbon cement). The adjacent exterior surface (S) following etching reveals very little surface topography, partly because of the exuding of lower molecular weight material expelled from the tapes during the compaction process [7]. This is an indication of molecular fractionation occurring during the melting and recrystallization processes associated with compaction.

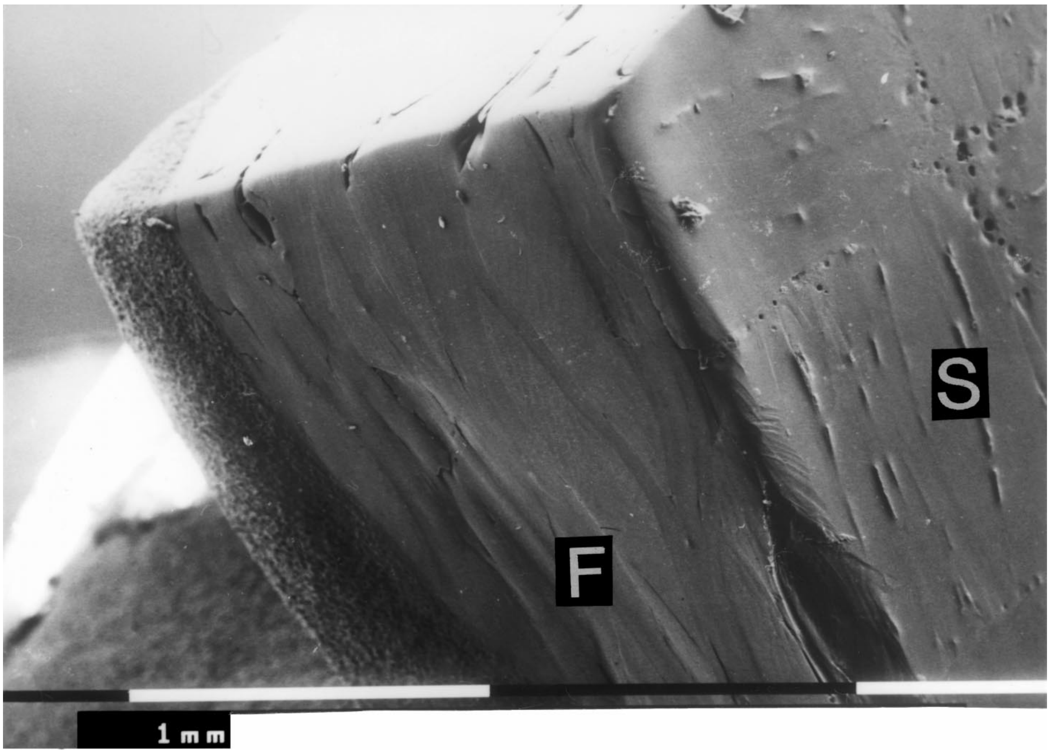


Figure 4 Overview of an etched sample compacted at a temperature of 184 °C. Note the different topography of the interior surface F, revealed by microtomy to the exterior surface S.

Figure 5 SEM micrograph of an etched sample compacted at 172 °C. Recrystallized material can be observed at a number of locations between adjacent tapes.

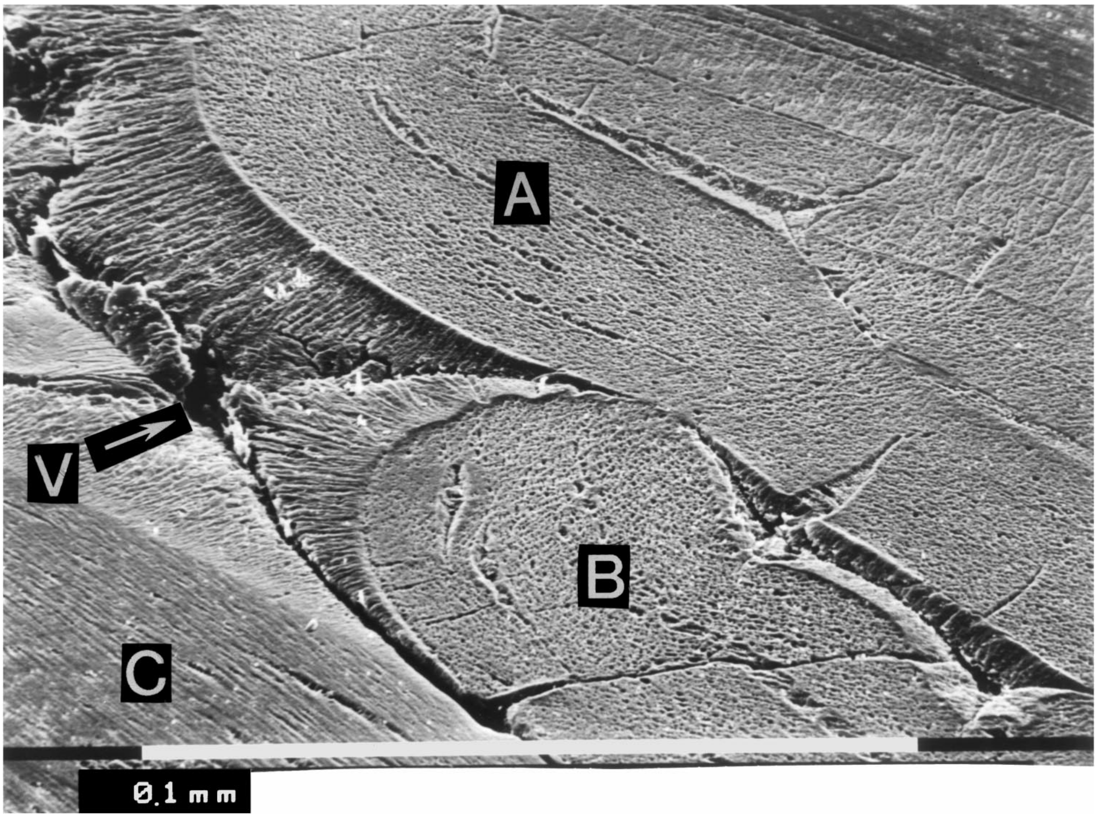


Figure 6 SEM micrograph of an etched sample compacted at 178 °C showing three adjacent fibres of differing orientation A, B & C. Note the two component nature of the compaction, containing original tape and recrystallized material. Full consolidation has not been attained at this temperature as can be seen by the presence of void, V.

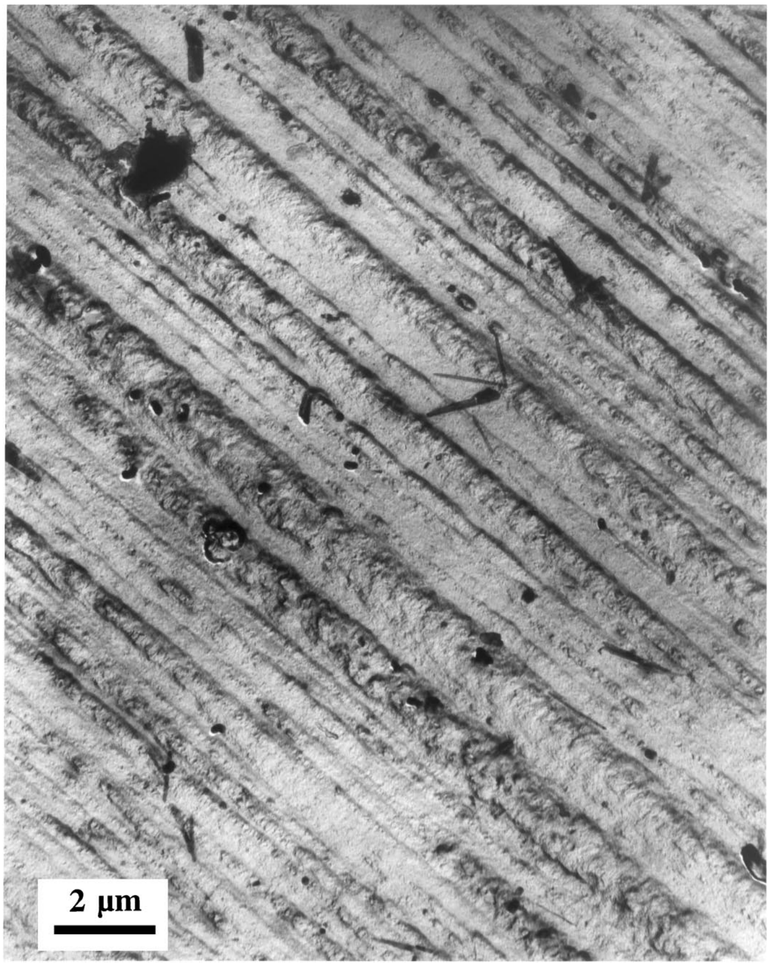


Figure 7 TEM micrograph of the etched internal tape structure following compaction at 184 °C. Note the presence of shish-kebab structures within the individual fibres, indicating internal melting and recrystallization from linear nuclei.

During compaction the tapes adopt a space filling arrangement, with significant tape deformation. The first observable effect with rising compaction temperature is to heal the cracks and for partial melting and recrystallization to occur between adjacent tapes; this behaviour can be observed for a compaction temperature of 172 °C in Fig. 5, especially at the lower right corner, although several inter-tape gaps have yet to be filled.

At a compaction temperature of 178 °C yet more material has become molten and produced a partly consolidated structure as seen in Fig. 6 where a large region of recrystallized material is present between three adjacent tapes of different orientation (A, B transverse to and C in the plane of the paper). It is noteworthy that while a significant proportion of material has been melted at this temperature, it is still insufficient to consolidate the structure completely, as indicated by the void, V, at the centre of this recrystallized region. This micrograph also reveals the internal textures of the polypropylene tapes, in both longitudinal and transverse section. The two tapes A and B emerging from the page are distinctly pitted, with regions of inhomogeneity across their width; additionally the cracks observed at lower compaction temperatures are now filled with recrystallized material. It appears that the recrystallized material which has nucleated on the tapes presented transversely has been etched to a lesser extent than the transverse tape structure itself, resulting in a pronounced lip. In this zone immediately adjacent to their nucleation site, the lamellae will be particularly tightly packed [8]. The effect is less obvious with the longitudinally oriented tape where the lamellae will be presented edge-on.

Compaction at 182 °C has previously been determined through both mechanical and morphological analysis as being the optimum compaction temperature. The structure and morphologies present at this compaction temperature have been discussed previously [4] and show that there is then just sufficient melting to allow the formation of a fully consolidated structure. The effects of still higher compaction temperatures involve recrystallization both within and between tapes.

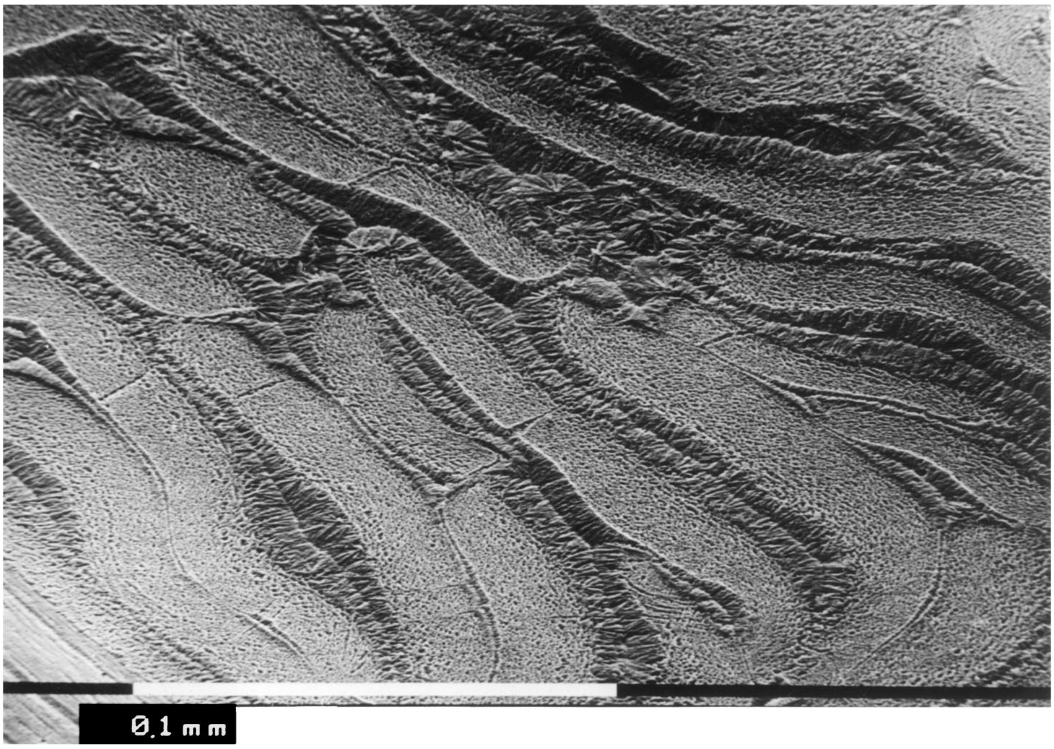
3.4. Intra-tape recrystallization

At a compaction temperature of 184 °C the internal morphology of the tapes reveals a two component structure. Fig. 7 shows etched longitudinal sections of a

Figure 8 TEM micrograph of etched recrystallized material between two longitudinally oriented tapes compacted at 184 °C. Note the highly aligned growth nucleating on the adjacent fibre (arrowed), and the difference in morphology at the meeting of adjacent growth fronts.

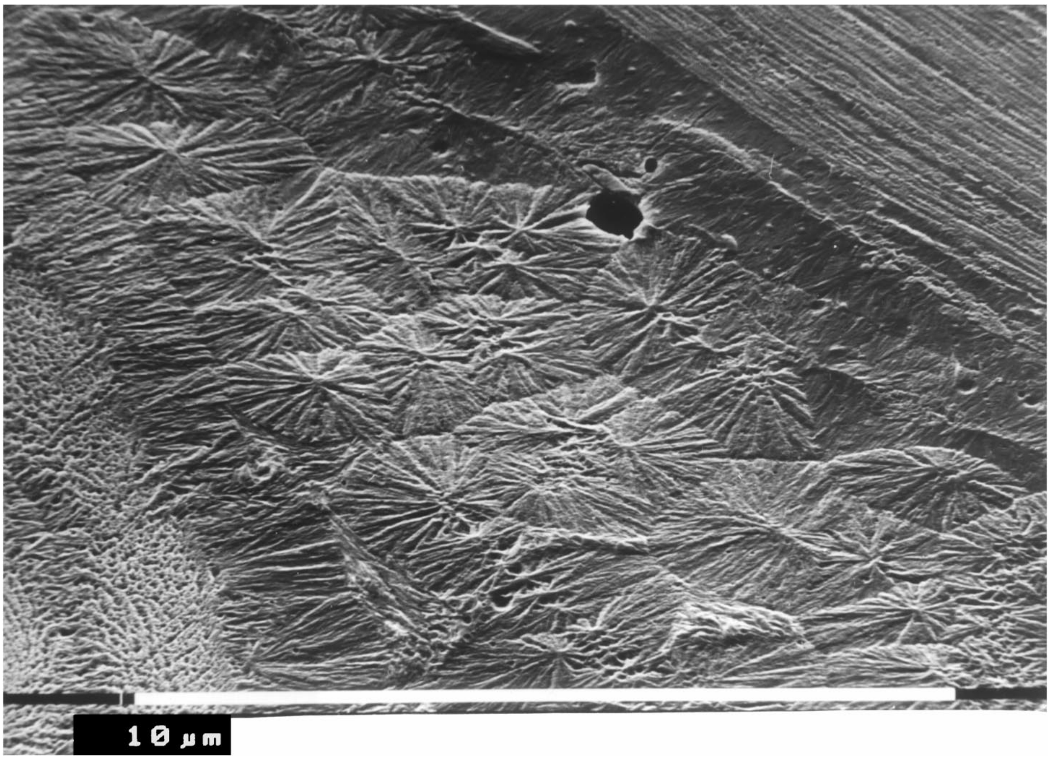
tape whose internal morphology is of shish-kebab type with material that has melted then recrystallized from adjacent original tapes and adopted the same c-axis orientation. This organization is related to the pitted structures observed in transverse tape sections (Fig. 3b) due to regions of reduced density which have greater free volume for the etchant to penetrate. The differential melting leading to the formation of a two component internal tape structure can be associated with the tape's entanglement network and the varying abilities of molecules to relax and melt under constraint. Without this constraint, the oriented tie molecules would be

(a)

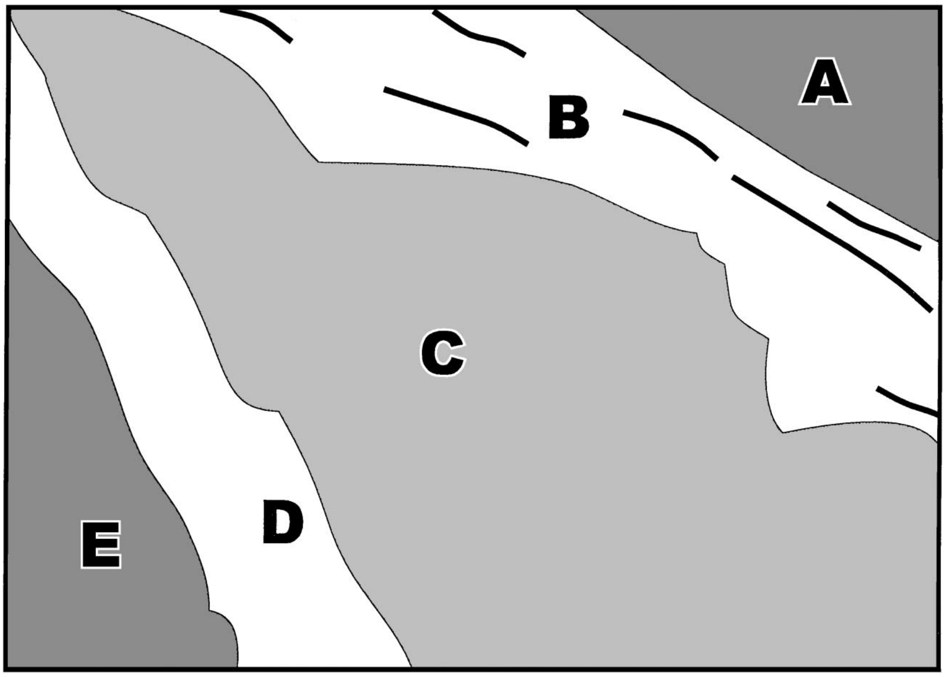


(b)

Figure 9 (a) SEM micrograph showing the degree of recrystallized material and tape structure remaining following compaction at 190 °C and etching. Here the contrast is such as to clearly reveal the fibrillar and recrystallized material following compaction, (b) higher magnification SEM micrograph showing the degree of consolidation following compaction at 190 °C and etching. Note the formation of end-on row structures which have formed in the middle of the large recrystallized area just above the centre, (c) SEM micrograph displaying end-on row structures present between transcrystalline regions and unmelted tapes and (d) diagram of the regions. (*Continued*)



(c)



(d)

Figure 9 (*Continued*).

converted in part to lamellar crystals, with a concomitant rapid decrease in modulus from about 147 °C [9]. The presence of this network in oriented polypropylene has long been inferred from mechanical studies, particularly creep measurements [10, 11]. Melting requires the presence of sufficient free volume to accommodate the associated decrease of density and begins, accordingly, either at external surfaces or internally at positions of excess free volume. Such are the lines observed in the initial starting material as longitudinal grooves along the sample (Fig. 3a). Molecules which are least constrained by the entanglement network can participate in melting in these regions progressively.

3.5. Inter-tape recrystallization

The edge-on lamellar profiles of the recrystallized material formed between two adjacent longitudinally arranged tapes can be seen in Fig. 8. Here the lamellae close to the nucleation site on the tape are all tightly packed and emerge approximately parallel to each other (arrowed). However as the crystallization process continues a degree of divergence is observed between adjacent lamellae, with curved lamellar profiles being common. Towards the centre of the recrystallized material the structure is much coarser, with a boundary region visible where the two impinging growth fronts meet (Fig. 8). This behaviour which differs from polyethylene [1, 2] where impinging growth fronts merge without discontinuity may well be due to rejected species of lower stereoregularity which impede crystallization.

At the highest compaction temperature studied, 190 °C, there are large areas of melted and recrystallized material evident throughout the sample. Fig. 9a shows the extent to which the original tape structure is still present with the inter-woven bundles clearly seen; those cut in longitudinal section appear grey in these imaging conditions while those cut transversely appear light and the recrystallized material appears black. This micrograph shows that while a significant proportion of the tapes have melted to consolidate the compaction much of the original tape structure remains. It is highly probable that what remains includes a large proportion of the entangled network of long molecules, and this will have an important bearing on retaining a significant fraction of the original tape's mechanical strength even after such extensive melting. On closer examination (Fig. 9b) it is clear that sufficient melt has formed to consolidate the structure, with no gaps at the joins between impinging growth fronts. The demarcation between the impinged growth fronts is, however, different from the situation with linear polyethylene where there was found to be lamellar continuity from one tape to its neighbour. In the present case it may be that there is a degree of segregated material at the growth front which tends to inhibit this process and could conceivably reduce the coherence of the boundaries.

Additionally at 190 °C a new feature of the compaction process becomes apparent. Instead of the recrystallized material nucleating only from adjacent tapes, there are now a number of row structures seen end-on in the centres of larger recrystallized regions. This behaviour can be seen at higher magnification in Fig. 9c, with regions diagramatically indicated in Fig. 9d. At top right A is a region of still unmelted tape in longitudinal orientation. From this a transcrystalline layer B is growing out, with a characteristically bland appearance because the lamellae are seen edge on. This layer is extended outwards by the presence of some unmelted remants of longitudinal fibres which are acting as nucleation sites further out in the melt. In the bottom left corner there is another pair of tapes E in transverse orientation, with a transcrystalline layer D which appears more rugged because the lamellae are seen flat-on. In the centre C there is a mass of individual rows displaying their characteristic spoke-like appearance of radiating flat-on lamellae [8] which, seen looking down the row axis, appear much more wheel-like than do spherulites. Row structures are known to form on linear nuclei, usually arising in polypropylene as a consequence of longitudinal flow which extends the underlying molecular network [12]. Here, the central location would be the site of maximum velocity when there is flow due to the application of pressure during the compaction process. As the spacing of rows does not vary laterally, it may well be that actual sites of nucleation are more dependent on surviving vestiges of the initial entangled molecular network. Although the orientation of this zone is more or less the same as that of the transcrystalline layer D, it appears as discrete from that one as from layer B, so it is unlikely to be simply an extension of the layer.

4. Conclusions

1. Compaction of woven polypropylene tapes is effected by the partial melting and recrystallization of polymer both within and outside the component tapes.
2. Optimum compaction is achieved when sufficient polymer melts just to fill all cavities and make the resulting self-composite a continuous material. At lower compaction temperatures not all voids are filled whereas higher compaction temperatures melt more material than is required.
3. The boundaries between impinged crystallization fronts are more marked than is the case for compacted polyethylene and may well be less coherent in consequence, this may well be due to the intervention of lower molecular weight and less stereoregular material.
4. At the highest compaction temperatures row structures form in the centre of the extensive regions of recrystallized material parallel to adjacent tapes because of flow in the molten polymer.

References

1. P. J. HINE, I. M. WARD, R. H. OLLEY and D. C. BASSETT, *J. Mater. Sci.* **28** (1993) 316.
2. R. H. OLLEY, D. C. BASSETT, P. J. HINE and I. M. WARD, *ibid.* **28** (1993) 1107.
3. M. I. ABO EL-MAATY, R. H. OLLEY, D. C. BASSETT, P. J. HINE and I. M. WARD, *ibid.* **31** (1996) 1157.
4. P. J. HINE, I. M. WARD and J. TECKOE, *ibid.* **33** (1998) 2725.
5. R. H. OLLEY and D. C. BASSETT, *Polymer* **23** (1982) 1707.
6. J. TECKOE, PhD thesis, University of Reading, 1998.
7. P. H. GEIL, "Polymer Single Crystals" (Interscience Publishers, New York, 1963) chap. iv, p. 269.
8. H. M. WHITE and D. C. BASSETT, *Polymer* **39** (1998) 3211.
9. K. YAMADA, M. KAMEZAWA and M. TAKAYANAGI, *J. Appl. Polym. Sci.* **26** (1981) 49.
10. J. DUXBURY and I. M. WARD, *J. Mater. Sci.* **22** (1987) 1215.
11. B. E. READ, G. D. DEAN and P. E. TOMLINS, *Polymer* **29** (1988) 2159.
12. M. J. FOLKES and D. A. M. RUSSELL, *Polymer* **21** (1980) 1252.

Received 28 September
and accepted 12 November 1998