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# The hot compaction of woven polypropylene tapes

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In this paper we describe the hot compaction of woven polypropylene (PP) tapes. It is shown that under suitable conditions of temperature and pressure, successful compaction is achieved by selective melting of the PP tapes. Mechanical measurements, combined with morphological studies, show that good tape to tape bonding, and good interlayer bonding, are achieved using an optimum compaction temperature of around 182 °C, while retaining a significant proportion of the original PP structure. Differential scanning calorimetry studies have shown that the compaction temperatures employed to produce a homogeneous coherent material have a significant annealing affect on the crystalline structure of the original drawn tapes, with a large change in the crystal size and a small increase in overall crystallinity (accompanied by a small increase in sample density). The mechanical properties of the compacted PP sheets show a combination of low density and good stiffness and strength. © *1998 Kluwer Academic Publishers*

## 1. Introduction

In the process of hot compaction, developed at the University of Leeds, high modulus, highly oriented thermoplastic fibres are processed to form thick section, homogeneous sheets without the need to introduce a second phase. In the original work on melt spun polyethylene fibres [1], it was shown that by suitable choice of processing conditions (i.e. temperature and pressure), a thin skin on the surface of each fibre could be 'selectively' melted, which on cooling recrystallized to bind the fibres together. It was established that good fibre to fibre bonding could be achieved by melting between 10 and 20% of the original fibre, with the result that the compacted sheets retained a significant percentage of the original fibre properties. Detailed structural analysis of the compacted melt spun polyethylene materials [2–4] showed an interesting microstructure with the original fibres surrounded by a 'matrix' of the melted and recrystallized material. This recrystallized phase was composed of lamellae growing out from the original fibre surface in row structures; a consequence of the number of nucleation sites available on cooling. This transcrystalline layer formed a strong fibre to fibre bond, such that subsequent failure was found to occur more readily in the fibres themselves.

In a number of subsequent papers we have investigated the applicability of the hot compaction process (British patent No. GB 2 253 420) to other high modulus thermoplastic fibres, namely polyethylene terephthalate [5], gel spun polyethylene [6] and polypropylene [7]. The polypropylene work employed unidirectionally arranged polypropylene fibres, and concluded that at the compaction temperatures used, up to 174 °C, selective surface melting was not achieved at a sufficient degree to develop any significant fibre to fibre bonding. The use of unidirectionally arranged fibres in the PP work meant using an open ended mould, and it was found that above 174 °C, the fibre assembly extruded from the mould. In the current study we have used woven PP fibrillated tape as the starting material, which allows a closed mould to be used, and compaction temperatures up to 190 °C to be employed. Compacted sheets have been manufactured at temperatures between 166 and 190 °C, and a variety of techniques have been used to investigate both the mechanical properties of the compacted materials and to determine the major compaction mechanisms. These have included flexural measurements of the stiffness and strength of the compacted sheets, morphological studies of the compacted sheet structure and compaction mechanisms and differential scanning calorimetry studies to evaluate melting behaviour and to investigate the significant annealing effects of the compaction conditions.

## 2. Experimental

The material used in this study was a woven polypropylene (PP) fibrillated tape (660 decitex) manufactured by Milliken Industries, USA. The weave style was nominally a plain weave (Style 1863) with each tow composed of bundles of between 10 and 15 tapes. The individual tapes were of the order of 200 μm wide

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and 25 μm thick, and were nominally isotactic polypropylene. The density of the individual PP tapes was measured by density column to be 906 ± 1 kg m$^{-3}$, and the tensile modulus, at a strain rate of 10$^{-3}$ s$^{-1}$, was measured to be 3.45 ± 0.05 GPa.

### 2.1. Compacted sheet manufacture

Compacted sheets, 2 mm thick, were manufactured in a 178 mm (7 inch) square matched metal mould using a hot press. First, the required number of layers (8 layers for a 2 mm thick panel) were cut from the woven PP cloth, and then stacked into the matched metal mould. In the initial trials, a soft aluminium sheet coated in mould release agent was placed either side of the stack of PP layers to aid release from the mould: subsequent tests showed that this was not required. The mould assembly was then placed into the hot press, which was set to the required compaction temperature. At this point a pressure of 2.8 MPa (400 p.s.i.) was applied to the mould assembly. The role of this pressure is twofold: to aid thermal contact and to restrain the fibres or tapes from shrinking. In previous studies a range of pressures have been used for this initial holding stage, from a low pressure of 0.7 MPa (100 p.s.i.) for the low shrinkage melt spun polyethylene fibre [1] to 2.8 MPa (400 p.s.i.) for the much higher shrinkage gel spun polyethylene fibre [6]. The polypropylene tapes used here showed a very high shrinkage at the compaction temperatures employed, and so a higher pressure was required for this initial holding stage.

Once the assembly reached the compaction temperature it was left for a further 10 min, after which a higher pressure of 7 MPa (1000 p.s.i.) was applied for 10 s before cooling the assembly to 100 °C under pressure and then removing it from the hot press. Samples were made at 166, 168, 170, 172, 176, 178, 180, 182, 184, 186, 190, 192 and 194 °C.

### 2.2. Differential scanning calorimetry (DSC)

As in our previous work, the DSC technique (using a Perkin Elmer DSC-Series 7) has been used extensively, both to examine the melting behaviour of the starting material, and hence decide a likely compaction temperature, and secondly to examine the melting behaviour of the compacted sheets, which sheds light on the compaction mechanisms and any annealing effects of the compaction process. In all cases the scanning rate was 10 °C min$^{-1}$, and all the measurements were made in a nitrogen atmosphere.

DSC has been used to examine the melting behaviour of the original PP tapes, both to ascertain the likely processing temperature range, and to assess the effects of constraint on the melting behaviour. This second aspect is important as the melting part of the compaction process is performed under a pressure of 2.8 MPa in order to restrain the PP tapes from shrinking, which in effect maintains them at constant length. Constrained melting is investigated by winding the PP tape around a piece of soft aluminium and tying off with a knot: this assembly is then placed into a DSC pan and tested in the normal way.

### 2.3. Morphological analysis-scanning electron microscopy (SEM)

For morphological analysis, small 2 mm thick blocks were cut from the compacted sheets. Internal surfaces were exposed by cryomicrotomy with a glass knife at −70 °C. Cuts perpendicular to the long axis of the block were produced. The nature of the woven tape structure dictated that the cuts in this plane created both transverse and longitudinal cross-sections of the average tape axis. The exposed surfaces were examined as prepared or, as in most cases, after etching with a permanganic reagent.

Experience has shown that different reagents are required to optimize detail in different components of texture. The reagent used in this work was 1% wt/vol potassium permanganate dissolved in an acidic mixture consisting of 10 volumes sulfuric acid, 4 volumes orthophosphoric acid (BDH reagent, minimum 85%) and 1 volume water, the sample being shaken for 1.5 h in the mixture. Recovery of the etched samples was as previously published [8], except that a small quantity of hydrogen peroxide was added to the chilled acid mixture, instead of being added as a second step.

Preparation of samples for SEM analysis involved mounting the etched blocks on SEM stubs and gold coating by sputtering in an argon plasma.

### 2.4. Mechanical measurements

For the previous studies, using unidirectionally arranged compacted fibres, we have usually measured the trade-off between the longitudinal modulus of the compacted sheets (a measure of the retention of the original fibre properties) and the transverse strength (a measure of the development of inter-fibre bonding due to selective melting). For this study, where we are dealing with woven bundles of tapes, we have measured the in-plane flexural modulus, which is taken as a measure of the retention of the original tape structure, and the in-plane flexural strength, taken as a measure of the development of interlayer and intertape bonding. Flexural tests were carried out on samples taken from sheets compacted at different temperatures. Samples, 5 mm wide, were cut from each compacted sheet, and tested in three-point bending following ASTM D790, using an RDP Howden servo-mechanical test machine: the nominal strain rate was 10$^{-4}$ s$^{-1}$.

The densities of the original tapes and the compacted sheets, were measured using a density column composed of a mixture of diglycidyl ether and isopropanol at 23 °C.

## 3. Results

### 3.1. DSC measurements

Fig. 1 shows a comparison of the unconstrained and constrained melting behaviour of the original PP tows

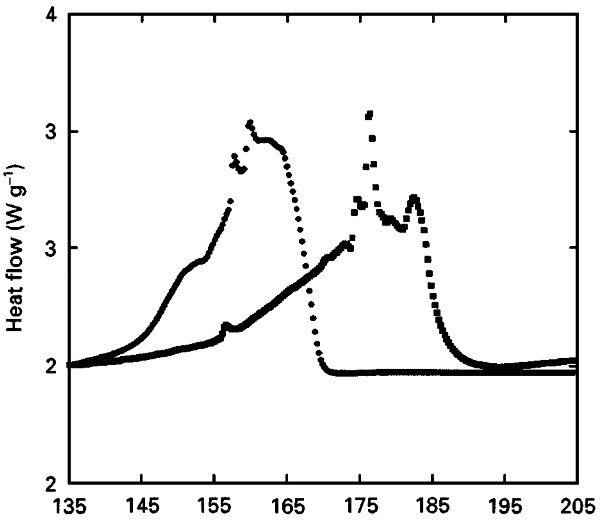


*Figure 1* DSC melting endotherms of the original polypropylene tapes both unconstrained (●) and constrained (■).

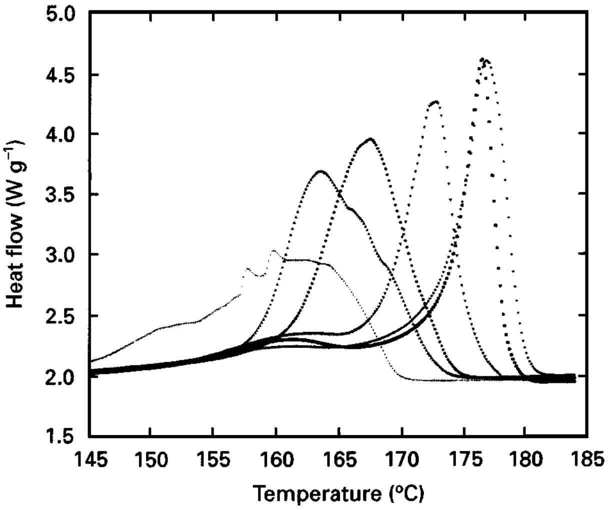


*Figure 2* DSC melting endotherms of compacted samples made at 166 (▲), 168 (●), 172 (▼), 178 (◆) and 184 °C (■), ( + ) original fibre.

(bundles of 15 tapes). There is clearly a large shift in the melting peak due to the effect of the constraint. The small sharp peaks superimposed on both curves, seen during the melting, are most likely due to individual tapes from within bundles melting early due to differences in constraint. It is interesting to note that the unconstrained melting endotherm shows evidence of a small peak at 152 °C with the main peak at 162 °C. Many authors [for example 9–11] have seen two peaks in the melting behaviour of unconstrained oriented PP and much work has been carried out to ascertain the origin of these two peaks. The behaviour seen here, for the unconstrained tapes, is similar to that from the work of Yadav and Jain [9] who reported the melting behaviour of a range of isotactic polypropylene fibres. In particular, for a draw ratio of 4 they found the first peak at 154 °C and the main peak at 164 °C. After subsequent experiments on the effect of heating rate on the position of these two peaks, they concluded that the lower peak was due to smaller and/or less perfect crystals, which is a conclusion shared by most of the previous work. Although outside the scope of this paper, DSC experiments at higher heating rates on the Milliken tape still showed two peaks, with both peaks moved to a higher temperature, confirming two crystalline populations rather than melting and recrystallization.

Compacted samples were then made over the temperature range suggested by the constrained melting peak shown in Fig. 1: samples were made at 166, 168, 170, 172, 176, 178, 180, 182, 184, 186, 190, 192 and 194 °C. Fig. 2 shows the melting endotherms of a representative proportion of these compacted samples. The differences in the melting endotherms can be separated into two aspects: first the desired melting and recrystallization which is the core mechanism of the compaction process, and secondly the large scale annealing effects of the compaction temperature on the crystalline structure of the polypropylene tapes, which can be viewed as a by-product of the compaction process.

Let us first consider the annealing effects of the compaction process. Although the most obvious aspect is the large shift in the position of the melting peak with compaction temperature, there is also a narrowing of the melting peak and a change in the total enthalpy of melting. Fig. 3a shows the peak melting point of each compacted sample plotted against the compaction temperature, while Fig. 3b shows the total enthalpy of the melting endotherm plotted similarly. With increasing compaction temperature the peak melting temperature rises from a value of 162 °C for the original tape, up to a peak value of 177 °C at a compaction temperature of 178 °C. The enthalpy similarly reaches a maximum value of 100 J g$^{-1}$ at this compaction temperature, up from a value of 86 J g$^{-1}$ for the original tape. Taking a value for the enthalpy of the 100% isotactic (α) crystalline material of 207 J g$^{-1}$ from the work of Bu *et al.* [12] gives the change in crystallinity from 42% for the original tape up to a maximum of 48% for the compacted sheets, which is a 6% increase. A shift in the melting peak is usually attributed to an increase in the crystal size and/or an increase in the perfection of the crystalline fraction, and has been reported by other authors during annealing studies of oriented PP [10, 11, 13–15]. In the work of Turley and Keskkula [14], they conclude that annealing polypropylene just below its melting point results in a better organization of the crystallizable portion of the structure. The previous studies, particularly Farrow [13] and Turley and Keskkula [14], also confirm that the refinement of the crystal structure due to annealing does not increase the crystallinity significantly, hence the emphasis in [14] on the 'crystallizable' portion of the structure.

The second aspect of the DSC endotherms shown in Fig. 2 are features associated with hot compaction, that is bonding of the PP tapes due to selective crystalline melting. In our previous studies, we associated the onset of successful hot compaction with a decrease in the enthalpy of the main crystalline melting peak associated with the original material, together with the appearance of a smaller lower melting point peak

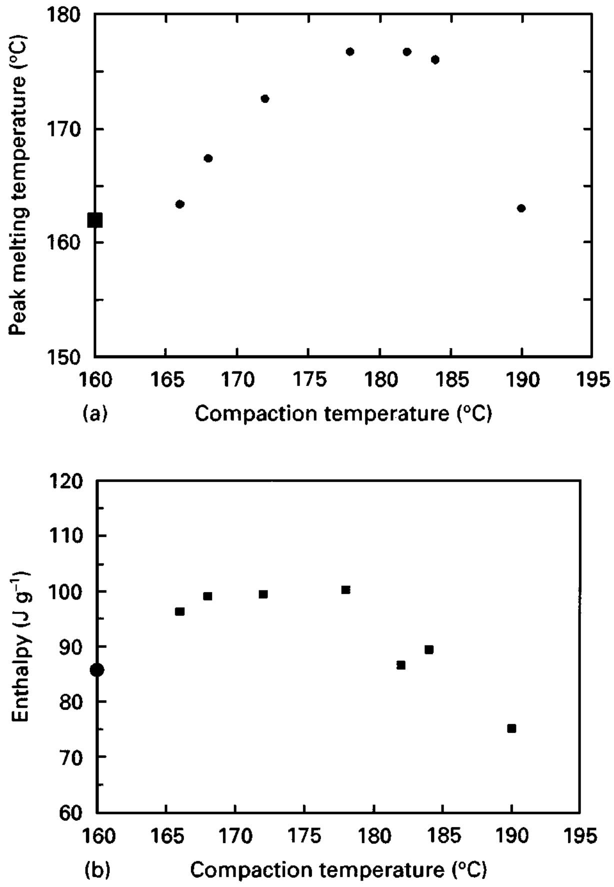


*Figure 3* (a) The peak melting temperature for compacted samples (●) versus the compaction temperature, (■) original fibre. (b) The enthalpy of melting for compacted samples (■) versus the compaction temperature, (●) original fibre.

which is associated with any melted and recrystallized material. Fig. 3b shows that the enthalpy begins to fall above a compaction temperature of 178 °C, suggesting that at this temperature significant crystalline melting begins to occur. As will be seen in a subsequent section, this is just below the temperature when the flexural properties show a significant rise. At this compaction temperature there is a clear lower melting peak very close to the position of the melting peak of the original unconstrained (and unannealed) tape, as shown in Fig. 2. This peak is also apparent at the lower temperature of 172 °C, and at the higher temperatures of 182 and 184 °C. As an example of the proportion of these two peaks, for the sample compacted at 178 °C, the first peak had an area of 17 J g$^{-1}$ while the area of the upper peak was 84 J g$^{-1}$: for the sample compacted at 184 °C the area of the first peak was 24 J g$^{-1}$ and the area of the second peak was 65 J g$^{-1}$.

As a summary of the changes which occur during compaction, Fig. 4 shows a comparison of the melting endotherms of the original unconstrained tapes and a sample compacted at 184 °C. As described above, the compacted sample shows a large shift in the position of the main melting peak, a narrowing of the main melting peak, and the appearance of a lower melting peak associated with melted and recrystallized material.

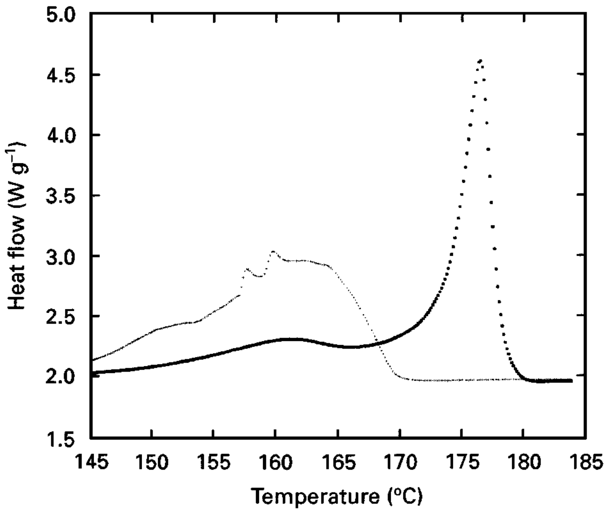


*Figure 4* A comparison of the DSC melting endotherm of a sample compacted at 184 °C (■) compared to the original fibre ( + ).

## 3.2. Mechanical tests

### 3.2.1. Flexural properties

Fig. 5a and b show the measured values of the in-plane flexural stiffness and the in-plane flexural strength of samples compacted between 166 and 194 °C. The variation of these two parameters with compaction temperature is very similar, with both increasing significantly at around 180 °C and reaching a maximum at 186 °C. The temperature at which the flexural properties begin to rise appreciably correlates well with the onset of significant selective melting as seen from the morphological studies. These results also correlate well with the previous study on unidirectionally aligned polypropylene fibres [8], where a maximum compaction temperature of only 174 °C was attainable, and it was shown that the mechanical properties were poor. The previous morphological studies also showed that selective melting of the polypropylene fibres did not occur at this temperature.

Returning to the results shown in Fig. 5, at low compaction temperatures, where significant selective melting does not occur, the polypropylene tape bundles are not well bonded to each other and the structure still contains voids: the mechanical properties are therefore poor. The mechanical properties rise to a peak at around 186 °C. At this temperature, the structure is homogeneous and well bonded, but above this temperature large scale melting occurs (as shown by a fall in the enthalpy of melting for samples compacted above this temperature – Fig. 3a) and so the mechanical properties fall. If we consider the optimum compaction temperature as a competition between developing good mechanical properties through selective melting, and losing the original structure of the polypropylene tapes, then a temperature of 182 °C would appear to be a good compromise.

### 3.2.2. Density measurements

Density measurements were carried out on the original tapes, and on a sample compacted at 182 °C, using

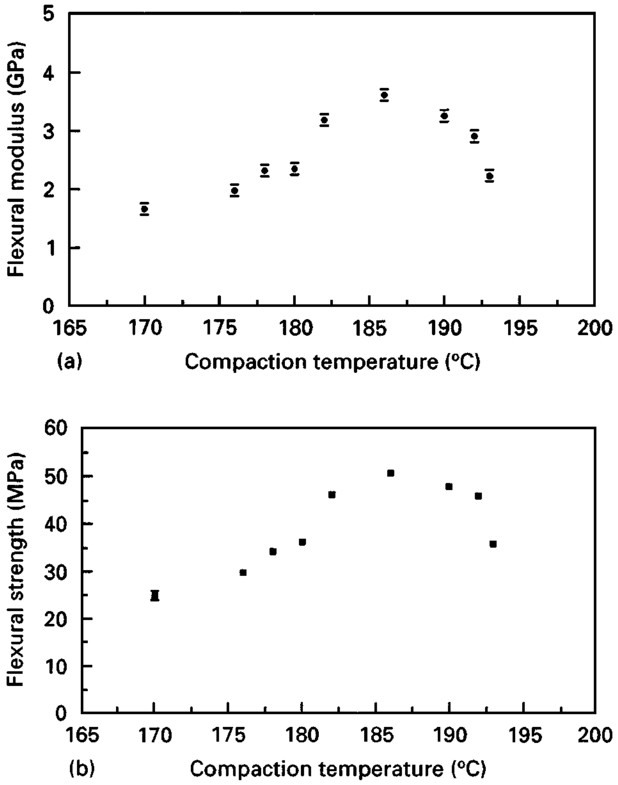


*Figure 5* (a) The in-plane flexural modulus of compacted samples versus compaction temperature. (b) The in-plane flexural strength of compacted samples versus compaction temperature.

a density column. The density of the original PP tapes was measured as 906 kg m$^{-3}$ while the compacted sample was 917 kg m$^{-3}$. Taking representative values from the literature for the crystalline and amorphous densities as 936 and 853 kg m$^{-3}$, predicts a change in crystallinity due to the compaction (annealing) process, of from 64% for the original tapes up to 77% for the compacted sheets, a rise of 13%. Although the absolute values of crystallinity are different from those determined from DSC measurements, the trend of the values, and the percentage change, are in good agreement (16% rise from DSC measurements, 20% rise from density measurements). Crystallinities determined by different methods are often in disagreement due to a number of factors. This calculation should be treated as an indication rather than an absolute, as the exact nature of the starting material (i.e. the tacticity index), and hence precise values of the amorphous and crystalline densities and the heat of enthalpy for the 100% crystalline material, are at present unknown.

### 3.3. Morphological analysis

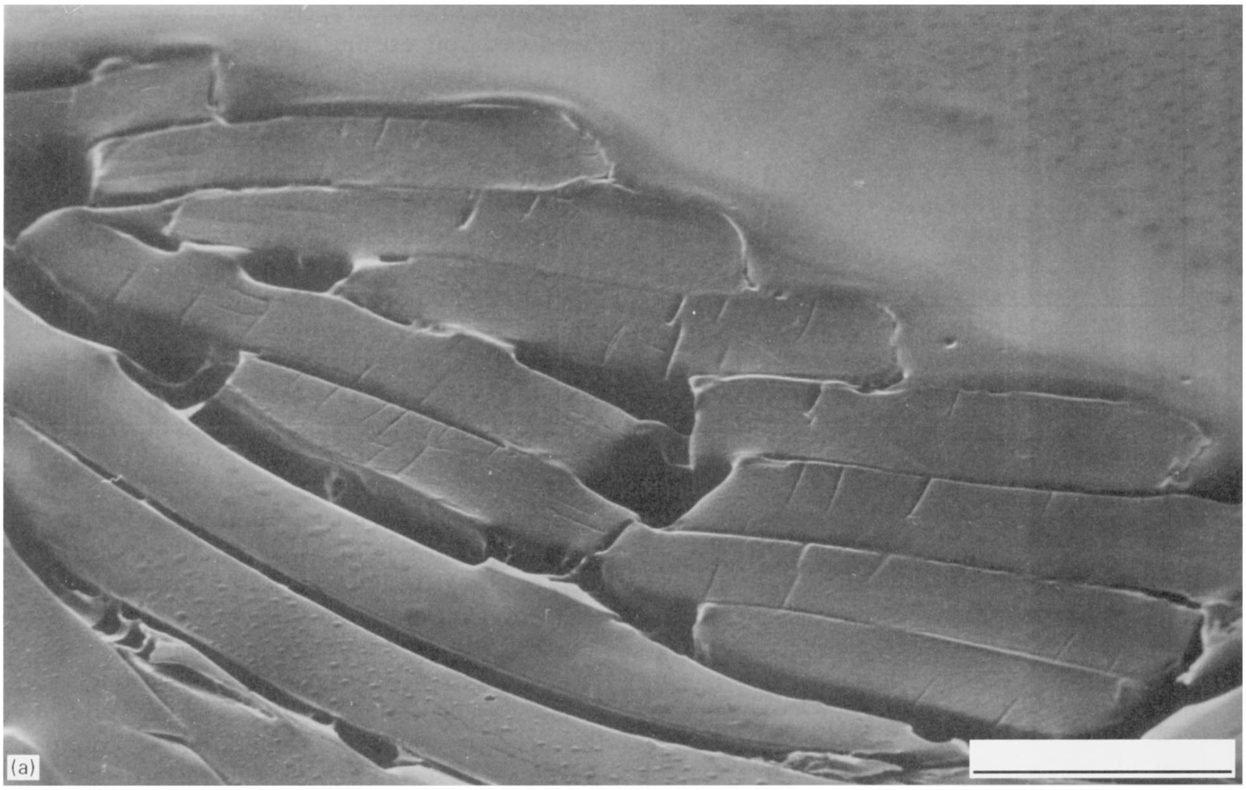
In this section we will show six representative SEM micrographs in order to discuss the morphological changes which occur due to the compaction process, in comparison with the DSC and mechanical results. A more detailed discussion of the morphological aspects of the compaction of these materials will appear in a subsequent publication.

The condition of the original tapes are shown in Fig. 6a and b. When the tapes are seen end-on, as in the centre of the Fig. 6a, cracks (which will have been developed from existing damage by etching) are present which have spread from the surface into the interior. They tend to be concentrated along one side of the tape as would be expected from surface tensile stresses caused by bending the tape about its long axis. The lower part of Fig. 6a shows the second component of the woven structure: here the tapes lie more or less parallel to the paper. Salient detail of the fine structure in this orientation is visible in Fig. 6b. There are longitudinal surface grooves, several micrometres long, parallel to the axis with some small point-like pits, all of which will have been accentuated by etching during sample preparation. Towards the right side of the upper tape is a kink band revealed by a surface step.

At low compaction temperatures (e.g. 168 °C – Fig. 7a) there is no sign of any recrystallized melt, either between the individual tapes, or between the bundles of tapes. Cracking from surfaces, as noted above in Fig. 6, is still present at a compaction temperature of 168 °C but may now extend across several tapes with some tendency to zig-zagging. The earliest signs of bonding are seen for a compaction temperature of 172 °C, as shown in Fig. 7b. This correlates well with the DSC results as it is at this temperature (Fig. 2) that the lower melting point peak; associated with melted and recrystallized material, first becomes apparent. For the most part, boundaries between tapes are discrete but the space between two tapes, just above the centre in Fig. 7b, has been filled in by the beginning of fusion. Also to be noted is the cross-texture (left of centre in Fig. 7b) developing within tapes viewed end-on which is similar to that noted in uniaxial polypropylene fibres compacted at similar temperatures and ascribed there to internal deformation mechanisms.

The extent of fusion increases with compaction temperature. Detail such as that of Fig. 8a (compacted at 178 °C) shows that the growth fronts of the recrystallized polypropylene growing from individual tapes do not always fuse well when they meet, reflecting, in part, the different crystallographic orientations of the adjacent tapes but possibly also the influence of rejected species carried along the growth front. A further possibility is that at this lower compaction temperature insufficient melt has been produced to fill all the available spaces between the tapes. Note also that etching has produced differences in level, with recrystallized material tending to stand out proud, especially when lamellae lie in the plane of the paper. The tapes themselves tend to have etched more quickly and deeply, at least partly as a consequence of their more open textures which have appeared at the higher compaction temperatures.

By 182 °C there is sufficient material, more or less, to fill all the internal spaces and so bind the tapes together. In Fig. 8b (compacted at 182 °C) one sees gaps filled both between near parallel longitudinal tapes and also between longitudinal and transverse orientations; the tape boundaries, however, remain clearly identifiable. Increasing the compaction temperature above 182 °C causes more of the original tape



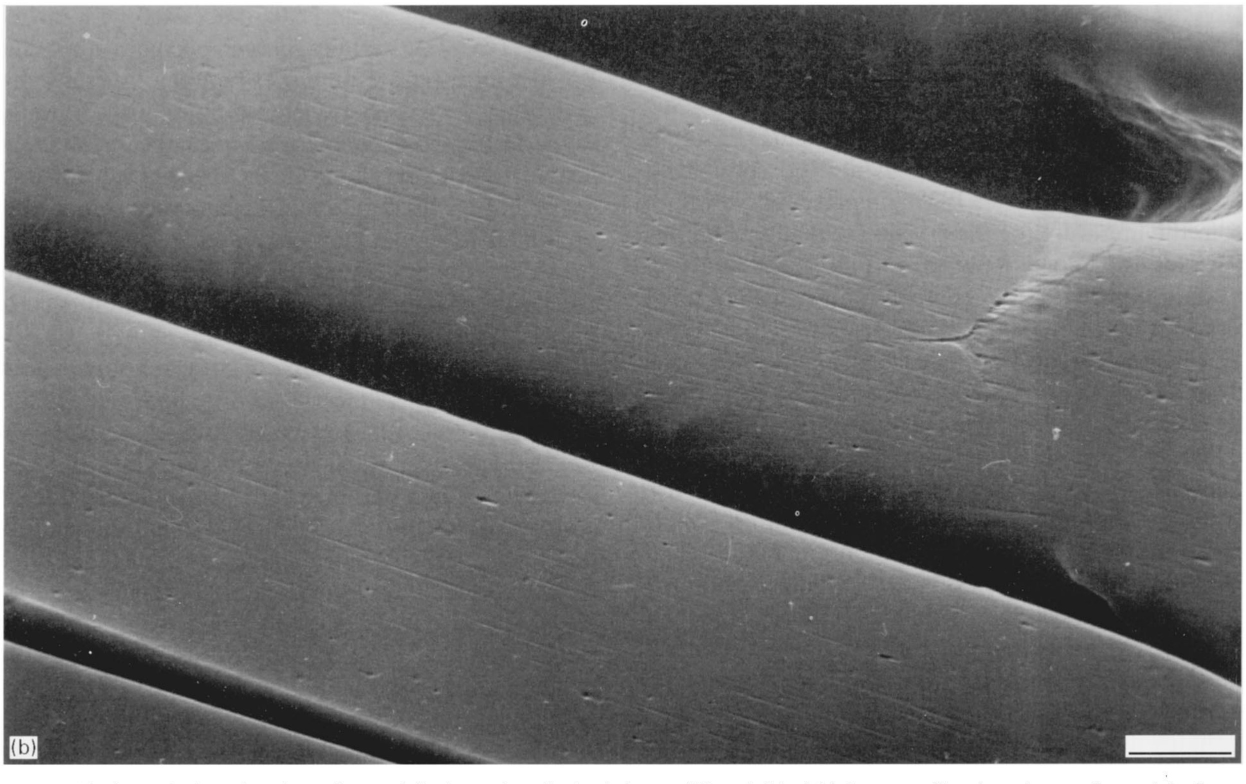


*Figure 6* (a) An etched section through an original tape bundle (scale bar = 100 μm). (b) A higher magnification picture of an original tape bundle (scale bar = 10 μm).

structure to be lost, eventually leading to a drop in the mechanical properties.

## 4. Discussion

The effects of the compaction process on the polypropylene tapes investigated in this study can be separated into two aspects. First, there is desired selective melting of the polypropylene tapes, which on cooling produces a transcrystalline layer which binds the bundles of tapes together and forms a coherent and well bonded structure. The optimum temperature, for the polypropylene tapes studied here, is around 182 °C where good in-plane mechanical properties are developed before a significant amount of the original oriented structure is lost.

The second aspect of the compaction process is the annealing affect on the crystalline regions of the

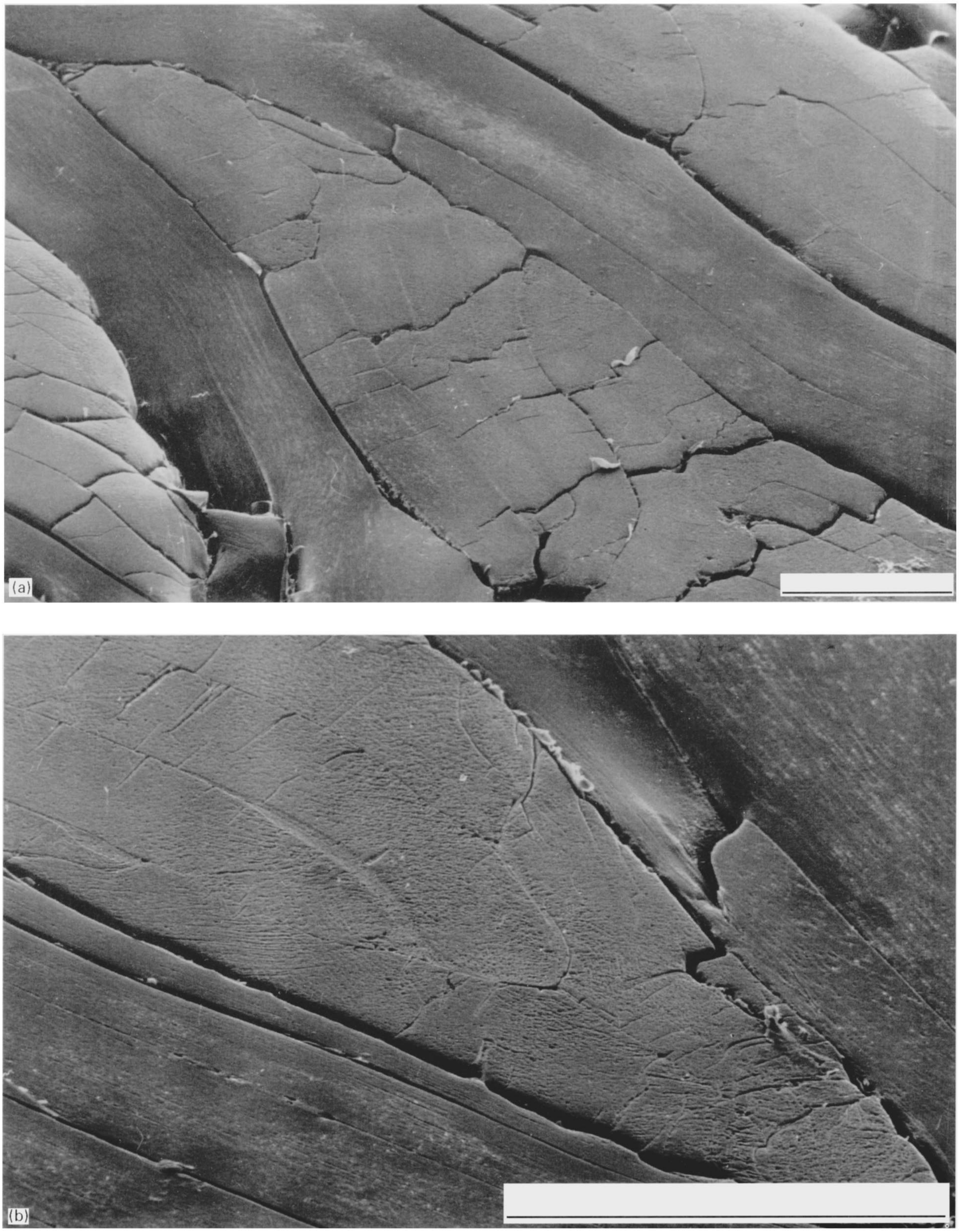


*Figure 7* (a) An etched section of a sample compacted at 168 °C (scale bar = 100 μm). (b) An etched section of a sample compacted at 172 °C (scale bar = 100 μm).

polypropylene tapes. DSC measurements on compacted sheets show that the annealing effect starts at a much lower temperature than the selective melting, with significant differences being measured at compaction temperatures of as low as 166 °C. Between 166 °C and the optimum compaction temperature of 182 °C, a large shift is developed in the peak melting position (of 14°) and the melting peak is considerably sharpened; there is also a 16 to 20% increase in crystallinity as measured by both DSC and density measurements over this temperature range. The changes in peak position and width are due to increased size and perfection of the crystalline regions of the original polypropylene tapes.

While the changes in the crystal structure with annealing are interesting, it is likely that they do not

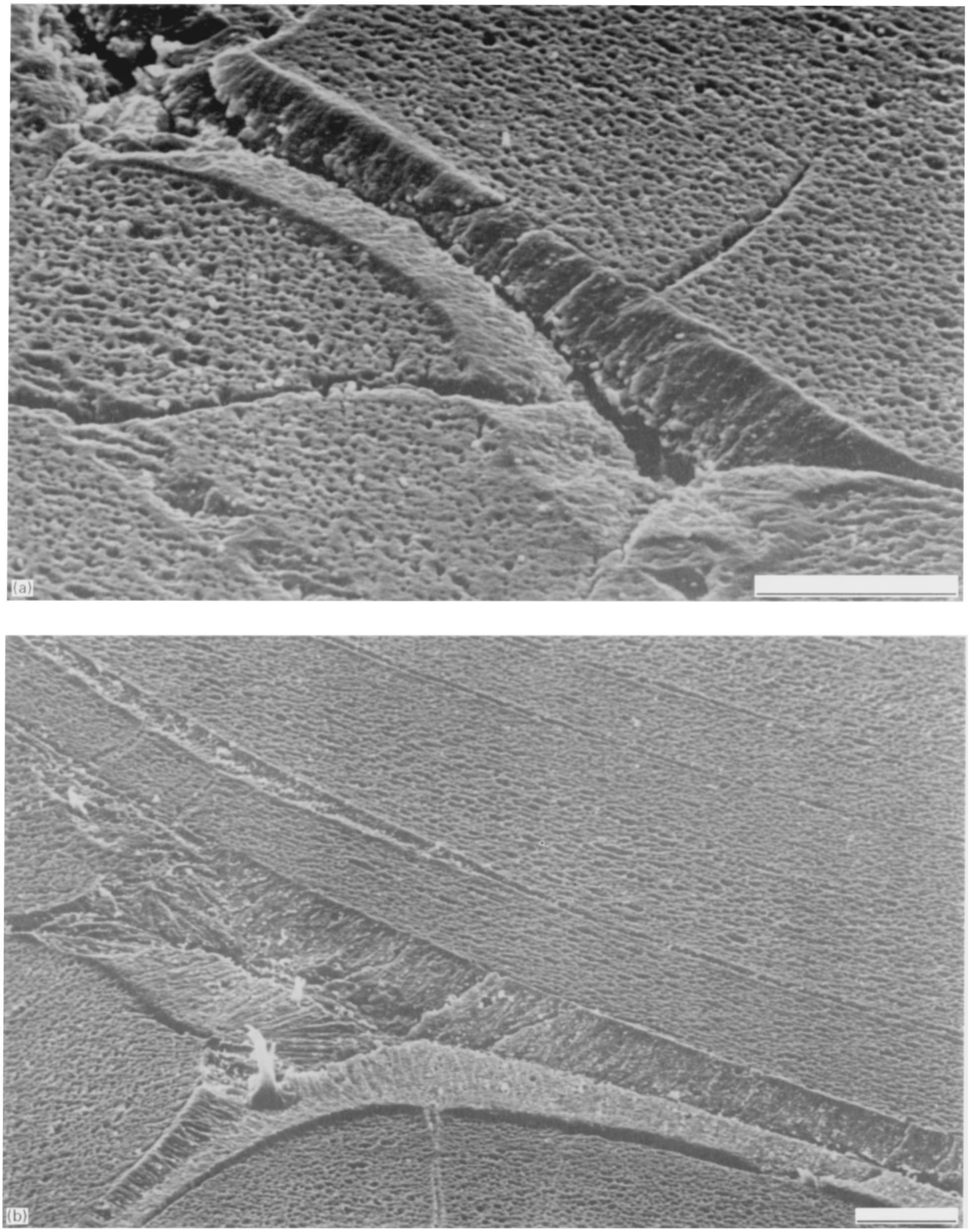


*Figure 8* (a) An etched section through a sample compacted at 178 °C (scale bar = 10 μm). (b) An etched section through a sample compacted at 182 °C (scale bar = 10 μm).

influence the mechanical properties of the compacted sheet significantly. This is because of the envisaged structure of the drawn polypropylene tapes, in which the fibrils consist of alternating layers of highly oriented cyrstalline lamellae and partially oriented amorphous material connected in series. This 'softer' phase, by virtue of being in series with the crystals, will greatly influence the axial stiffness of the drawn tapes. This is in direct contrast to highly drawn polyethylene fibres, where the structure is similar to a fibre reinforced composite with the lamellar structure reinforced by long crystals, the so called intercrystalline bridges [e.g. 16], which are stable right up to the onset of melting. In consequence, highly drawn polyethylene fibres can be taken to their melting range, and compacted without any noticeable shrinkage and without loss of orientation.

## 5. Conclusions

In this paper we have described how woven drawn polypropylene tapes can be successfully compacted at an optimum temperature of 182 °C. At this temperature, a homogeneous and well bonded sheet is produced by a process of melting and recrystallization, while a significant fraction of the original structure is maintained. The compaction temperatures employed in this work have an additional large annealing affect on the original polypropylene tapes, leading to a 20% increase in crystallinity. Morphological studies confirm that at the optimum compaction temperature, the good mechanical properties are due to the development of a transcrystalline layer between tapes and tape bundles.

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