On Morphologies Developed during Two-Dimensional Compaction of Woven Polypropylene Tapes

T. AMORNSAKCHAI,[1]* D. C. BASSETT,[1] R. H. OLLEY,[1] P. J. HINE,[2] I. M. WARD[2]

[1] J. J. Thomson Physical Laboratory, Whiteknights, Reading RG6 6AF, United Kingdom

[2] IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, United Kingdom

Received 15 November 1999; accepted 14 February 2000

ABSTRACT: The microstructure of compacted woven polypropylene cloths prepared at their optimum compaction temperature of 184°C has been examined. Details of transverse and longitudinal cross-sections have been revealed by permanganic etching and observed with scanning electron microscopy. The original cloth was found to contain perpendicular cracks and biconical defects reported previously in other systems. After compaction, the cloth bonded together to form a thick solid sheet, with a melting point raised for the residual material but reduced for the recrystallized component. The higher melting regions form a continuous three-dimensional network with linear traces in a longitudinal section, in agreement with recent observations of fiber structure. Recrystallization occurs both within and externally from tapes: where parallel tapes meet, transcrystalline layers emanate from tape surfaces, with a distinct line where the two growth fronts meet. In some more extensive recrystallized regions row structures are formed, probably indicating local flow during compaction. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 787–793, 2000

Key words: polypropylene tapes; electron microscopy; permanganic etching; composites; morphology

INTRODUCTION

In recent years, a number of articles have described the process of hot compaction,[1–4] whereby high modulus thermoplastic fibers are treated at a suitable temperature and pressure to form thick section sheets that show comparable properties to the original fibers.[5] The process was originally developed for high modulus polyethylene fibres,[1] but more recently has been extended to the more cost-effective polypropylene (PP) fibers and woven PP tapes with a wide range of potential applications. The temperatures at which unidirectional compaction of PP fibers can be carried out are severely limited,[3] and for higher temperature compactions with more effective consolidation it is necessary to use two-dimensional cloths.[4] Our interests in this area can be divided roughly into two parts. One is the processing and mechanical properties of the compacted sheet, which includes thermoformability of the hot compacted sheets and the suitability of the hot compaction technology to a continuous process;[6] the other being morphological studies using microscopy to understand and explain the mechanical results.[2,7,8]

A range of PP tapes and fibers of different stiffness and orientation has been studied.[6] It was found that the material that offers the best balance between cost and performance is a woven slit film manufactured by Amoco UK, grade 6082, plain weave. This type of material has been found

---

Correspondence to: R. H. Olley.

* On leave from Dept. of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand.

Journal of Applied Polymer Science, Vol. 78, 787–793 (2000)

to retain the highest proportion of its mechanical properties after compaction.[6] The mechanical properties of the compacted sheet of this material can be found elsewhere.[6] This article presents the corresponding morphological features and their implications. Comparison with parallel work on a similar material manufactured by Milliken[4] shows that there are certain morphological features peculiar to the Amoco film, which are retained in the compacted product.

EXPERIMENTAL

The woven slit film of PP used in this study (normally used as geotextile) was grade 6082, plain weave, manufactured by Amoco UK. This material contains approximately 0.5% carbon black, an additive whose effect is difficult to predict in advance. Because the choice of particle size and structure can lead to advantageous or deleterious effects in regard to mechanical properties and to degradation, different grades can act either as sensitizers or stabilizers.[9,10]

To establish the optimum compaction temperature, samples were manufactured over a range of temperatures from 177 to 187°C, using a single-pressure compaction process. The required number of layers of the woven PP cloth were placed into a matched metal mold (four layers of cloth equate to 1 mm of compacted sheet). The mold assembly was then placed into a hot press set at the compaction temperature and the pressure of 2.8 MPa (400 psi) applied to the mold (termed the compaction pressure). Once the mold assembly has reached the compaction temperature the assembly was left for a further 10 min to allow even melting throughout the layers of woven PP, then cooled at ~2 K · min^{-1} to 100°C, removed from the press and air cooled.

In the compaction process there is always a trade-off between the development of interfiber or intertape bonding due to selective surface melting, and a fall in the mechanical properties of the final sheet due to a loss of molecular orientation associated with this melting. In the previous compaction studies, where unidirectionally arranged fibers were used, this "optimum compaction temperature" was established by measuring the longitudinal modulus of the compacted sheets in the fiber direction and the transverse strength of the sheets perpendicular to the fiber direction. For the current study with woven tapes, the optimum temperature was found by measuring the in-plane flexural modulus of the sheets and their interlayer adhesion. The flexural modulus was measured according to ASTM D790, at a strain rate of 10^{-4} s^{-1}. The interlayer adhesion was measured using a T-peel test (after ASTM D1876), employing samples compacted from two layers of the compacted woven material. During lay-up, a piece of aluminium foil is placed between the two layers of cloth, at one end of the sample; after compaction this foil acts as a starter crack for the peel test.

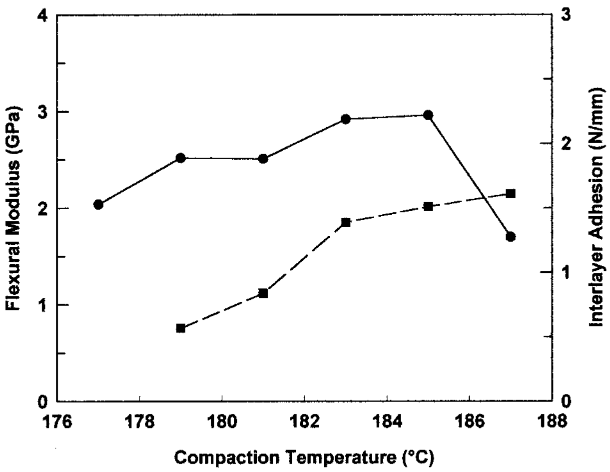

Figure 1 Effect of compaction temperature on flexural modulus (solid line, circles) and interlayer adhesion (broken line, squares).

For morphological studies, a piece from a compacted sheet was cut perpendicular to the plane of the sheet using a glass knife on a cryomicrotome at a temperature of −70°C. This exposes both transverse and longitudinal sections of differently oriented tapes within the same specimen. The specimen was then etched for 1 h in a 1% solution of potassium permanganate in a 10 : 4 : 1 mixture (by volume) of concentrated sulphuric acid, orthophosphoric acid (85%), and water.[11] Etched surfaces were examined using scanning electron microscopy (SEM) after gold coating.

RESULTS AND DISCUSSION

Mechanical

The results of the mechanical tests are shown in Figure 1. As the compaction temperature was increased, the flexural modulus gradually rose reflecting increased bonding and then fell sharply above 185°C when widespread melting occurred.

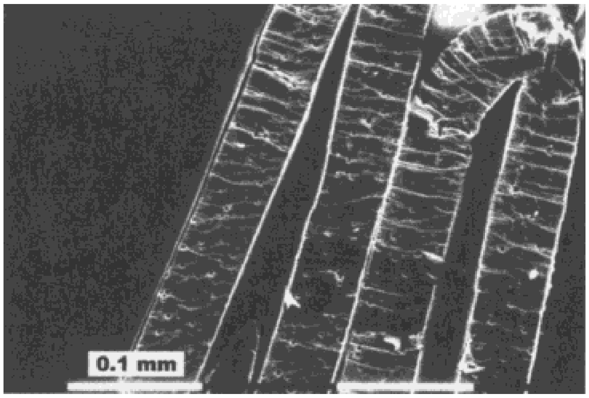

Figure 2 SEM of an etched transverse section of original PP tape with etched voids and cracks.

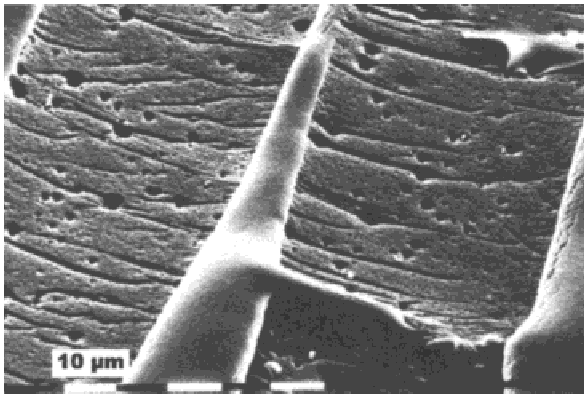

Figure 3 Higher magnification of Figure 2 showing detail of the cracks running perpendicular to the plane of the tape and the pitted nature of the surfaces.

The interlayer adhesion increased steadily with compaction temperature. From these tests, the optimum temperature was considered to be 184°C, 2 K higher than for the previous material;[4] samples made at this temperature were used for the subsequent morphological studies.

The raw material for this compaction, namely Amoco 6082, differs from the PP braid Milliken 1863 used in the series of compactions examined previously,[4] where each unit of the weave consisted of approximately 15 tapes. Here, the units are two pieces of slit film that are generally either doubled over or folded into three. Following previous work with polyethylene fibers and their compactions, we may anticipate that in addition to general common features there will also be significant differences of detailed morphology dependent first upon the process by which the fiber was originally manufactured,[12] but also on the details of compaction, as was found especially between the melt-spun[2,8] and gel-spun[13] polyethylene fibers. Differences between the present and former polypropylene tapes are highlighted below.

Uncompacted Cloth

Figure 2 shows the uncompacted cloth, embedded in block copolymer. These particular tapes are seen in transverse section, one being folded over. The main features to note are the lines running across the section, which are much more abundant than in the parallel work on the Milliken material.[4] Commercial and laboratory PP tapes are often found to be weak in this direction, giving rise to a raffia-like fibrillation.[14] In the present case, it is probable that the lines are (possibly incipient) cracks that have been opened up chemically by the etchant, as has been observed in some commercial fibers,[3] although with careful preparation this weakness may be avoided.[15] Small holes are also observed, but it is not immediately obvious whether these are actual voids in the material or are etched out pockets where less resistant material has congregated. Voids have been found in other tapes after etching,[14] but were not observed in the parallel work on the Milliken material.

At the higher magnification of Figure 3, a general stippled texture is seen but the grooves and larger holes are clearly differentiated. The geometry of the holes becomes clearer in longitudinal section, as in Figure 4, which reveals them to be biconical similar to those previously observed in other types of drawn PP.[15]

Compacted (184°C) Material

At low magnification (Fig. 5), the interwoven bundles of tapes in a compaction are clearly seen.

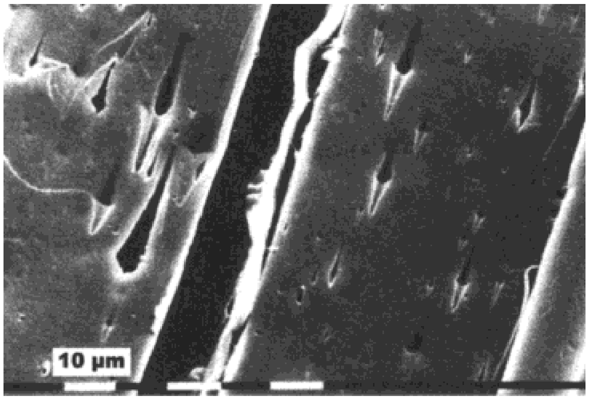

Figure 4 SEM of an etched longitudinal section of original PP tapes showing biconical defects.

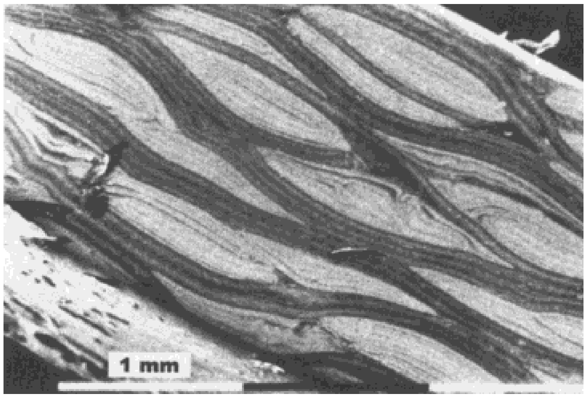

Figure 5 Low-magnification SEM of etched cut surface of the compacted sheet showing the woven structure of the original cloth.

Those cut longitudinally appear dark, those cut transversely appear light, a differentiation similar to that observed in the Milliken material but probably more pronounced, even allowing for variations in SEM technique between different operators. At higher magnification, the holes observed in the uncompacted material are seen again in Figure 6 in both longitudinal (corners) and transverse (center diagonal) sections, and appear to have conserved, more or less, their number and volume. Holes are present in the boundaries between tapes: where a recrystallized zone is absent (arrowed), this might simply be due to incomplete compaction, but where they occur in zones of recrystallized melt (Fig. 7, arrowed), their origin must be different. It is possible that after heat treatment the original holes may be filled with liquid low molecular weight material, which in early observations of PP heated near to its melting point, of many specimen types, it has been seen to migrate out from the main specimen to the surface or periphery of the specimen.[16,17] This effect is generally much more pronounced in highly oriented specimens such as tapes, and has been observed in detail in films stretched biaxially at elevated temperatures in a semimolten state,[18] suggesting either a much stronger thermodynamic driving force in oriented systems, or that the work applied during the compaction process provides the necessary free energy for a segregation process analogous to reverse osmosis. This latter suggestion has been invoked to account for the migration of the lower molecular weight tail of ultrahigh molecular weight polyethylene (UHMWPE) into the gaps between particles during the consolidation of this material for hip cups,[19] a feature previously observed during the consolidation of UHMWPE in general.[20] This type of migration is much more pronounced in PP than in polyethylene.

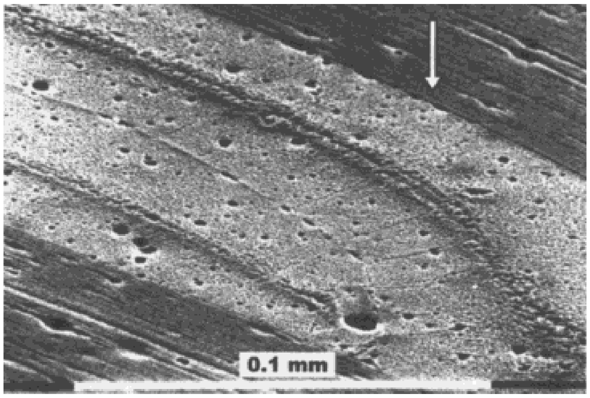

Figure 6 SEM of an etched compacted sheet showing the two different characters of boundaries between transversely oriented tapes, i.e., with and without the presence of recrystallized material. Etched voids are present in both cases. Small voids between tapes are arrowed.

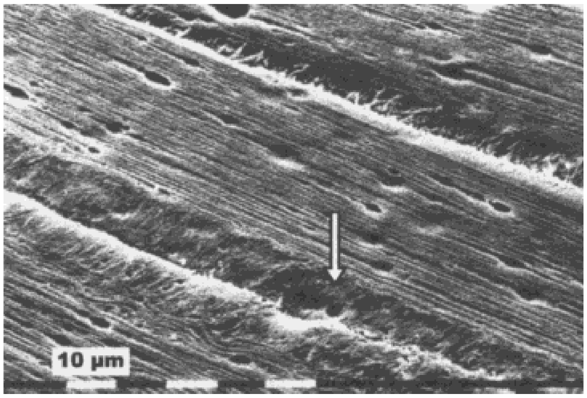

Figure 7 SEM of an etched compacted sheet showing melting and recrystallized material between two longitudinally oriented tapes. Note the coarsened surface texture of the longitudinal fibril as compared with that seen in Figure 3, and the void (arrowed) in the recrystallized melt.

Turning to the basic structure of the fibers themselves, one observes that their texture has been coarsened by annealing, relative to the original cloth illustrated in Figures 3 and 4. There is a great increase in the overall contrast of etched transverse sections (Fig. 6), with a smaller increase for the longitudinal section (Fig. 7). Melting has not been uniform through an entire fiber but, as has also been observed for various ad-

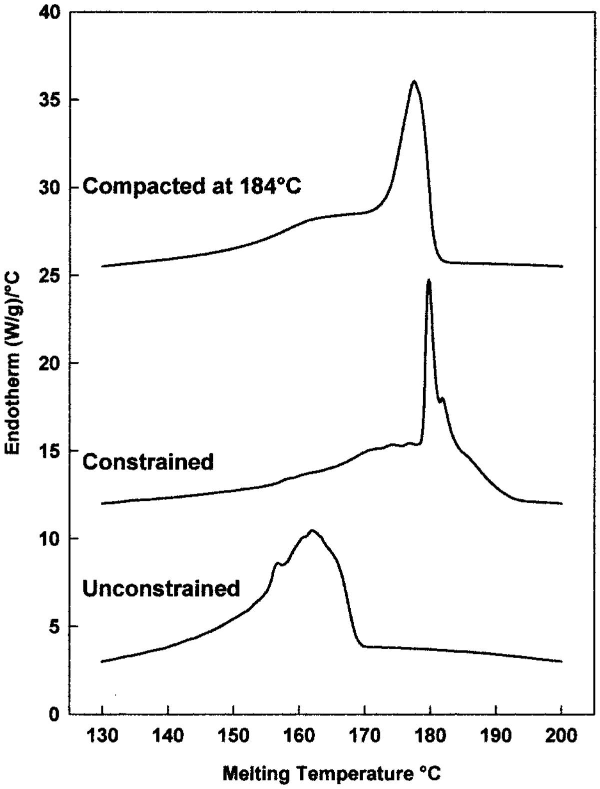

Figure 8 DSC traces of Amoco PP (bottom) original tape unconstrained (middle) original tape constrained and (top) material compacted at 184°C.

vanced polyethylene fibers,[21] a structure of parallel linear traces is developed in longitudinal sections that are the locations of the higher melting material. As with previous observations on polyethylene, this appearance results from the intersection of the surface with an extended molecular network, probably involving the longest molecules.[12,21] Although there has been considerable transformation of the structure, voids are still present but are rounded out somewhat in comparison to the original biconical shape. Along the top edge of the bottom fiber in Figure 7, there is a region of sinusoidal traces adjacent to the more usual linear ones. This not only illustrates the integrity of these high melting regions but is also suggestive of local buckling in what would have been a partly molten recrystallization zone.

This morphological differentiation is accompanied by a very substantial increase in the main DSC melting point of the compacted material as opposed to the precursor (Fig. 8). An increase in the melting point could be observed either due to an increase in crystalline perfection following the annealing, or to a decrease in the entropy of the oriented melt in a constrained sample. Such an increase is, in fact, seen if the original tape is melted under constraint. It is certain that any constraint imposed on the compacted specimen in the DSC pan is considerably less than this, because the higher melting peak refers to material that was still solid at 184°C while the material was constrained during the compaction. So it is considered that the upper peak relates to perfected material; the peak at 164°C is from the recrystallized material, as discussed previously,[4] where the latter temperature is typical for polypropylene crystallized from the melt. Such endotherms are similar to those found in compacted polyethylenes.[1]

The morphology giving optimum properties is once again that in which the original intertape cavities are just filled, in accordance with earlier findings for both polyethylene and PP compactions.[1,2,4,22] Unlike the former, however, the joins between recrystallized growth fronts remain evident, rather than being subsumed into a continuous lamellar array, as Figure 9 shows very clearly. The pleated tape seen in transverse section, in the center of this figure, retains a triangular void at the center of the pleat from which runs a detectable boundary between the inner surfaces of the pleat until these diverge. Beyond this point recrystallized fronts are present with ~40 μm on, a void where three fronts have met. Note also the three-way impingement of transcrystalline material in recrystallization of melt issuing from a longitudinal tape (top) and two sections of the same pleated transverse tape. The star-shaped impingement at the bottom right has formed from only two tapes, but both of these

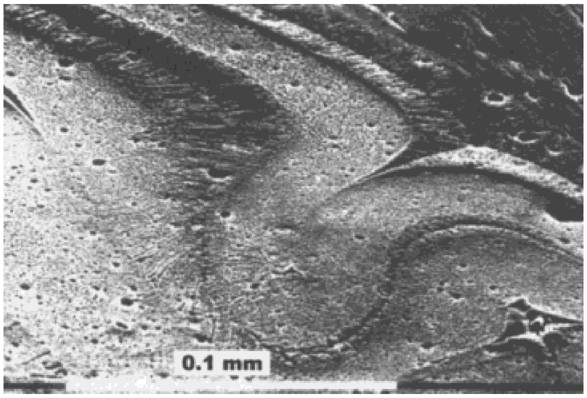

Figure 9 SEM of an etched compacted sheet showing the nature of the recrystallized geometries especially in relation to the pleated sheet at the center.

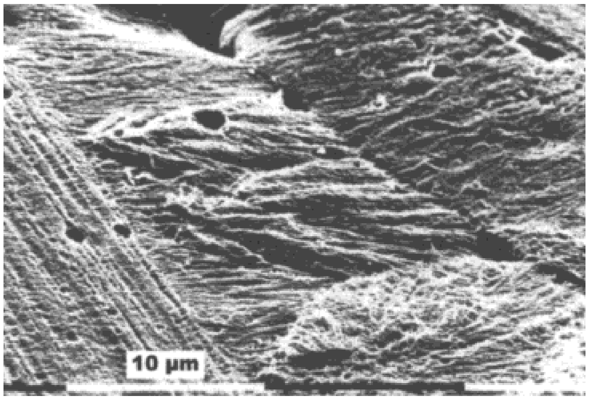

Figure 10 SEM of an etched compacted sheet showing melting and recrystallized material at the interface of longitudinally oriented tapes showing a combination of transcrystalline structure on the longitudinally oriented tape (lower left) and the comet-like appearance of row nucleated structures.

have buckled to produce effectively four growth fronts. These are instances of the diversity of ways in which the compaction process can accommodate irregularities in the packing of the original material, which undoubtedly contributes to the success of the process.

As observed previously, transverse sections of the tapes are etched more than recrystallized zones whose lamellae will be flat-on. Moreover, the α-polypropylene structure that develops will be rather rigid because of interlocking crosshatching that will tend to maintain differences in angle between separate growth fronts from different surfaces. This is the probable explanation for the retention of the initial geometry of growth that is a major contributor, in addition to the presence of exuded polymer, to the clear association of growth front and its surface of origin. In compacted polyethylene, by contrast, the memory of growth fronts is largely lost because flexible lamellae from different fronts join smoothly when they meet.[2] Figure 10 reinforces this point from a longitudinal perspective. Recrystallization has proceeded out from the tape in the lower left corner with lamellae edge-on, but diverging from separated nuclei, a morphology that suggests that the **b** axis is normal to the page. The boundary between this zone and its counterpart from above not only has a fair proportion of etched voids but also reveals that both zones have retained their initial planar geometry so that they have met inclined at the corresponding angle.

Finally, Figure 11 shows both the detail of a boundary between two tapes in transverse section and the cratered nature of such etched surfaces. In the boundary region are row structures, identified by their spoke-like appearance, in accordance with other work.[23] As suggested previously,[22] their presence is likely to result from a degree of flow parallel to the tapes during compaction.

The cratered surface structure, within which there are larger etched voids, reveals the intrinsic lateral network characteristic of highly oriented polymers that gives rise to the linear traces seen in Figure 7 and elsewhere. Its origin has been proposed[23] to be the extension of an entangled molecular network during processing from which further crystallization nucleates. The geometry and comparative rigidity of the network has the consequence that subsequent growth will tend to create a negative pressure as the polymer shrinks as it solidifies without a source of additional melt. Excess free volume ensues, in turn allowing greater penetration of the etchant and producing a cratered surface.

CONCLUSIONS

1. The morphology of compacted PP tapes giving optimum mechanical properties is that in which just sufficient material melts to fill all interstices between tapes and recrystallizes to improve transverse strength.
2. Boundaries between adjacent tapes generally remain discernible after compaction, whether or not material has melted and recrystallized between them, and are prone to

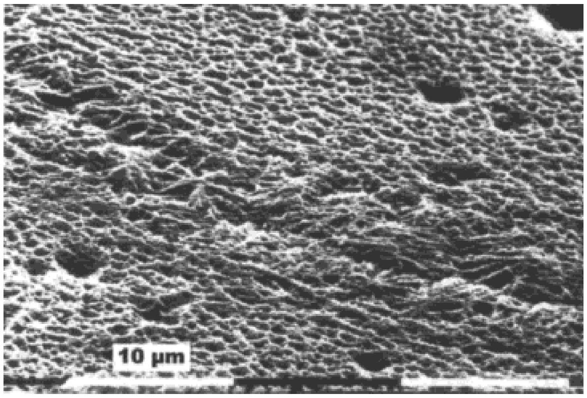

Figure 11 SEM of an etched compacted sheet showing detail of the cratered transverse surfaces. Note the presence of end-on row structures in the recrystallized material between the two tapes.

display etched voids in either case. These voids may be a legacy of exuded polymer of low tacticity while the rigidity of the cross-hatched α-phase tends to preserve the initial geometry and prevent smooth joining at interfaces.

3. Melting occurs both within and between tapes. The former is a consequence of the intrinsic lateral ordering found in highly oriented systems related to nucleation on an entangled molecular network during formation of the tapes.
4. Before processing, these particular tapes contain voided regions which may be filled with air or possibly low tacticity PP. These regions are retained in the compacted material, although losing their characteristic biconical shape.

REFERENCES

1. Hine, P. J.; Ward, I. M.; Olley, R. H.; Bassett, D. C. J Mater Sci 1993, 28, 316.
2. Olley, R. H.; Bassett, D. C.; Hine, P. J.; Ward, I. M. J Mater Sci 1993, 28, 1107.
3. Abo El-Maaty, M. I.; Olley, R. H.; Bassett, D. C.; Hine, P. J.; Ward, I. M. J Mater Sci 1996, 31, 1157.
4. Hine, P. J.; Ward, I. M.; Teckoe, J. J Mater Sci 1998, 33, 2725.
5. Br. Pat. No. GB 2 253 420.
6. Hine, P. J.; Bonner, M.; Brew, B.; Ward, I. M. Plast Rubber Comp Proc Appl 1998, 27.
7. Kabeel, M. A.; Bassett, D. C.; Olley, R. H.; Hine, P. J.; Ward, I. M. J Mater Sci 1994, 29, 4694.
8. Kabeel, M. A.; Bassett, D. C.; Olley, R. H.; Hine, P. J.; Ward, I. M. J Mater Sci 1995, 30, 601.
9. Horrocks, A. R.; Miraftab, M.; Mwila, J. In Geosynthetics: Applications, Design and Construction; De Groot, M. B.; Den Hoedt, D.; Termaat, R. J., Eds.; Balkema: Rotterdam, 1996, p. 851.
10. Mwila, J.; Miraftab, M.; Horrocks, A. R. Polym Degrad Stabil 1994, 44, 351.
11. Shahin, M. M.; Olley, R. H.; Blissett, M. J. J Polym Sci Polym Phys Ed 1999, 37, 2279.
12. Abo El Maaty, M. I.; Olley, R. H.; Bassett, D. C. J Mater Sci 1999, 34, 1975.
13. Yan, R. J.; Hine, P. J.; Ward, I. M.; Olley, R. H.; Bassett, D. C. J Mater Sci 1997, 32, 4821.
14. Horrocks, A. R.; D'Souza, J. A. Polym Degrad Stabil 1994, 46, 181.
15. Abo El Maaty, M. I.; Bassett, D. C.; Olley, R. H.; Dobb, M. G.; Tomka, J. G.; Wang, I. C. Polymer 1996, 37, 213.
16. Padden, F. J.; Keith, H. D. J Appl Phys 1959, 30, 1479.
17. Geil, P. H. Polymer Single Crystals; Interscience Publishers: New York, 1963, p. 267.
18. Olley, R. H.; Bassett, D. C. J Macromol Sci Phys 1994, B33, 209.
19. Olley, R. H.; Hosier, I. L.; Bassett, D. C.; Smith, N. G. Biomaterials 1999, 20, 2037.
20. Shahin, M. M.; Olley, R. H.; Bassett, D. C.; Maxwell, A. S.; Unwin, A. P.; Ward, I. M. J Mater Sci 1996, 31, 5541.
21. Teckoe, J.; Bassett, D.C.; Olley, R. H. Polym J 1999, 31, 765.
22. Teckoe, J.; Olley, R. H.; Bassett, D. C.; Hine, P. J.; Ward, I. M. J Mater Sci 1999, 34, 2065.
23. White, H. M.; Bassett, D. C. Polymer 1998, 39, 3211.