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The development of morphology during hot compaction of Tensylon high-modulus polyethylene tapes and woven cloths

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

The development of morphology in tapes and woven cloths of oriented melt-spun Tensylon polyethylene has been studied both before and after hot compaction over a range of temperatures below and above the optimum. For both the unidirectional fibres and the woven cloths, the optimum temperature was found to be where approximately 30% of the original structure was lost which, for Tensylon tapes, was ~2 K below the point of major crystalline melting, giving a processing window roughly twice as wide as for other previously studied polyethylene materials. Transverse sections show a two-component morphology after etching of cratered ribbons emerging from a flat, relatively featureless landscape. This morphology disappears at the highest temperature studied when the longitudinal morphology consists of oriented walls from which transcrystalline units have grown during cooling. Morphological comparison with other polyethylenes and their compactions places Tensylon behaviour alongside Dyneema, Spectra and Tekmilon rather than the melt-spun Certran. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Hot compaction; Self-reinforced composites

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1. Introduction

Polymer compaction is an emerging technology whereby fibres or tapes of a single polymer can be bonded into continuous single-polymer composites. These not only retain much of the properties of the original fibres or tapes but also bring much-improved cohesion. Although the idea of single polymer composites is not new [1], a particular compaction process has been developed at Leeds, initially for melt-spun fibres of polyethylene [2] to give unidirectional sheets, since when the process has been extended to polypropylene [3] and other polymers [4] and to two-dimensional tapes and cloths [5]. The major feature of the process developed at Leeds, is that it uses only a single highly oriented component as the starting point and by utilising suitable conditions of temperature and pressure, forms a consolidated single polymer composite. The majority of the other published work embeds the oriented component in a matrix of a similar polymer.

In a previous paper [6], we described an investigation into the hot compaction behaviour of Tensylon, a new commercial highly-oriented and ultra-high modulus polyethylene tape. This material compacts very well, producing exceptional properties with strength similar to gel-spun fibres. The optimum processing conditions were first established then the mechanical properties of the optimum samples were contrasted with other hot compacted PE materials, notably melt-spun Certran fibres and gel-spun Dyneema and Spectra fibres. Qualitatively, compaction proceeds in Tensylon much as in the other polyethylenes studied previously with the advantage of a wider processing window, twice as wide as found for previous materials. The purpose of the present investigation was to investigate the morphology of Tensylon tapes in both unidirectional and woven arrangements, compacted below, at and above the optimum compaction temperature, with a view to greater understanding of the compaction process.

2. Experimental

2.1. Materials

The high-modulus polyethylene studied, Tensylon, was

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Table 1
Mechanical properties of compacted samples taken from a previous publication [6]

Specimen no.	Compaction type	Compaction temperature (°C)	% Oriented remaining	Longitudinal modulus (GPa)[a]	Transverse modulus (GPa)[a]	Transverse strength (MPa)[a]
A	Original Tape	–	–	88	–	–
B	Unidirectional	151.6	91	69 ± 7	1.9 ± 0.1	6 ± 0.5
C	Unidirectional	152.0	88	60 ± 4	3.3 ± 0.3	9 ± 0.7
D	Unidirectional	152.9	63	58 ± 3	2.4 ± 0.1	26 ± 2
E	Unidirectional	154.1	33	45 ± 2	2.1 ± 0.1	24 ± 2
				In-plane modulus (GPa)	In-plane strength (MPa)	Peel strength (N/10 mm)
F	Woven cloth	153	66	30 ± 2	400 ± 20	9 ± 1.1

[a] Testing strain rate ($10^{-3}\ \mathrm{s}^{-1}$).

manufactured by Synthetic Industries, USA: this material is a flat tape, 2.1 mm wide and 70 μm thick.

2.2. Production of compacted sheets

Compacted samples were made for both a unidirectional arrangement of tapes and using woven tapes: full details are given in a previous publication [6]. For unidirectional samples, tapes were wound around a former and placed into a mould, while for woven samples, the required number of woven layers were cut and then placed into the mould. In either case, a thermocouple was placed in the centre of the tape assembly to monitor the process temperature and the technique used was a single pressure process. The thermocouple output was connected to a Comark KM 1242 recorder allowing 0.1 °C accuracy. The calibration of the recorder and thermocouple were routinely checked using boiling water (100 °C) and an ice/water mixture (0 °C). Once assembled, the mould was placed into a hot press set at the required compaction temperature and a pressure of 400 psi was immediately applied. The dwell time at the compaction temperature was 10 min, and samples were removed after cooling to 90 °C.

2.3. Mechanical properties of compacted sheets

The measurement of the mechanical properties of compacted Tensylon sheets, for both unidirectional and woven tapes, has already been described fully in a previous paper [6]. The role of the mechanical tests was to aid the establishment of the optimum compaction conditions, as well as giving an indication of the mechanical performance of these new materials. For unidirectional samples this was achieved by contrasting the modulus along the tape direction (longitudinal) with the transverse strength perpendicular to the tape direction. The optimum temperature was chosen as the point where good bonding (i.e. a high transverse strength) was achieved for the minimum loss of the original oriented phase, as given by the longitudinal modulus. For the woven samples a similar determination was carried out, but here contrasting the in-plane modulus with the interlayer peel strength, again examining the trade-off between the development of bonding and the loss of the original oriented phase. For reference the main results from the previous paper are repeated in Table 1. These results established that the optimum compaction temperature was ~153 °C, where the percentage of surface melting (~30%) was sufficient to provide good bonding without substantial loss of the original oriented phase.

2.4. Specimen preparation for microscopy

To produce surfaces for etching, specimens were sandwiched between two sheets of Kraton® block copolymer whose inner surfaces had been softened with toluene: the entire sandwich was left to dry at least overnight. The specimens were then mounted on a Bright microtome with Cryo-M-Bed mounting medium (TAAB Laboratories Equipment Ltd, www.taab.co.uk) frozen with solid carbon dioxide, and surfaces were cut open using either a diamond knife (for sections transverse to the orientation direction, including woven specimens) or a glass knife (for longitudinal sections) set at 10°.

Etching was carried out with a published permanganic reagent [7] consisting of 1% w/v potassium permanganate in a mixture of 10 vol concentrated sulfuric acid, 4 vol orthophosphoric acid (min 85%) and 1 vol water. The etching time was 2 h, after which the specimens were recovered by the published procedure [7].

All specimens were sputter coated with gold and examined under a Phillips 515 SEM. All were mounted at either 0°, or more often were rotated with their length at 45° on the screen, then tilted 45° for better contrast and to display structures both parallel and perpendicular to the specimen thickness equally.

3. Results and discussion

3.1. Raw material

The morphology of the original Tensylon tape before any compaction treatment but after cutting and etching is

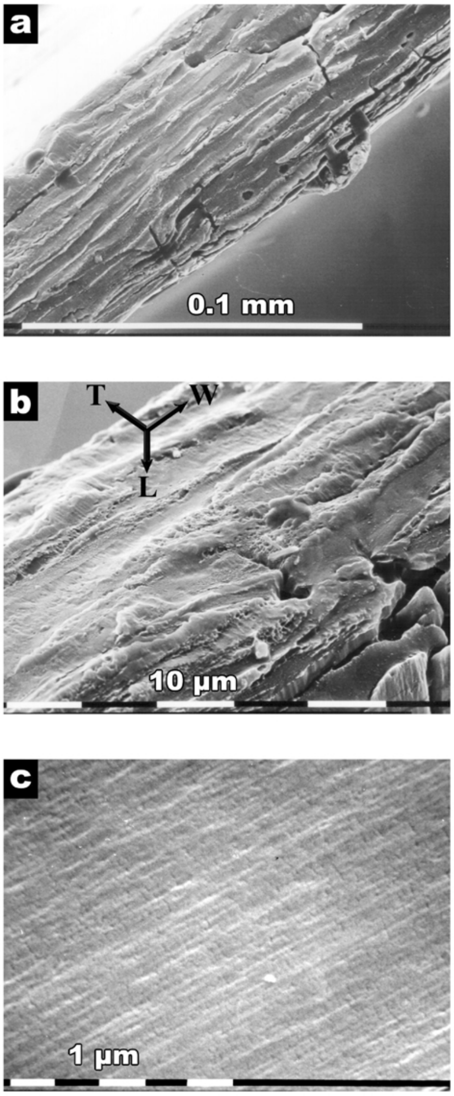

Fig. 1. Original tape (a) transverse, flat-on; (b) transverse, tilted; (c) longitudinal.

shown in Fig. 1. In transverse section, notwithstanding the difficulties of cutting such a high-modulus material, which even using a diamond knife tends to leave the surface badly damaged, features are seen (Fig. 1(a)) which are organized into 'ribbon-like' subunits approximately 30 μm along the width of the tape and ~6 μm across its thickness. In Fig. 1(a) the width of the tape and the cutting direction both run from bottom left to top right, while its thickness runs from bottom right to top left. More, but also more confused, detail is present in the tilted section of Fig. 1(b) in which certain features can be taken to be genuine, since they or their derivatives are present also in the compacted materials discussed later. While much of the material has etched to a rather bland surface, albeit with transverse ripples in places arising from microtome damage, the impression of subunits remains. The cracking observed goes in two directions. All cracks (which may have been opened up or widened by the etching) travel deep into the length *L* of the fibres: this is to be expected, as such highly oriented materials often show a raffia-like fibrillation. However, some cracks travel across the thickness *T* of the tape, while there is a more general propensity for cracks to travel along the width *W*. This direction is the one to be expected if the tape is indeed made up of ribbon-like units, and the fibrillation would lead to a raffia-like structure, as seems to be the case at bottom right where the etched tape appears to be breaking up into these components. In addition, there are regions where the surface shows small craters similar to those observed in the compacted materials and various high-modulus polyethylene fibres.

The longitudinal cut and etched section of Fig. 1(c) shows mainly a long linear texture with, at this magnification, a definite hint of transverse, presumably transcrystalline lamellar units which, however, are not visible in the original tape at any lower magnification.

3.2. Unidirectional compactions

Previous studies have established that the optimum compaction of Tensylon, in terms of the best balance of mechanical properties, occurs at 153 °C [6]. As with previously studied materials, examination of unidirectional samples of parallel tapes compacted slightly below and above this temperature yields useful information on the compaction process. Transverse cut surfaces of such samples, which have a moderately reduced longitudinal modulus, etch in a more regular fashion than did those of the original tapes and reveal pertinent detail. For samples made below the optimum temperature, both specimens B (151.6 °C) Fig. 2(a) and C (152.0 °C) Fig. 2(c) are very similar in appearance with a two-component morphology of highly cratered features standing proud of a more uniform and flatter landscape. DSC experiments confirmed a very similar fraction of melted material in these two samples (Table 1). At higher magnification, Fig. 2(b), the cratered regions are seen closely to resemble transverse views of other high-modulus polyethylene materials [8]. The intervening low lying flatter regions have etched at a faster rate but have no clear pedigree. There is no indication of two components in previous X-ray examination or thermal analysis. On the contrary, such tapes are single textured and highly oriented with an apparently single melting peak. These findings remove two possible causes of differential etching, namely differences in orientation and lamellar thickness leaving greater porosity and penetrability to the etchant as the most probable cause of the greater attack. The origins of this must lie in the fabrication history, possibly relating to the condition prior to the imposition of high orientation. Height differences disappear in the normal view of Fig. 2(d) which emphasizes the relative arrangement of the two components, showing that they are arranged similarly to the original ribbon-like subunits, some of which may, however, have merged into each other under the compaction process.

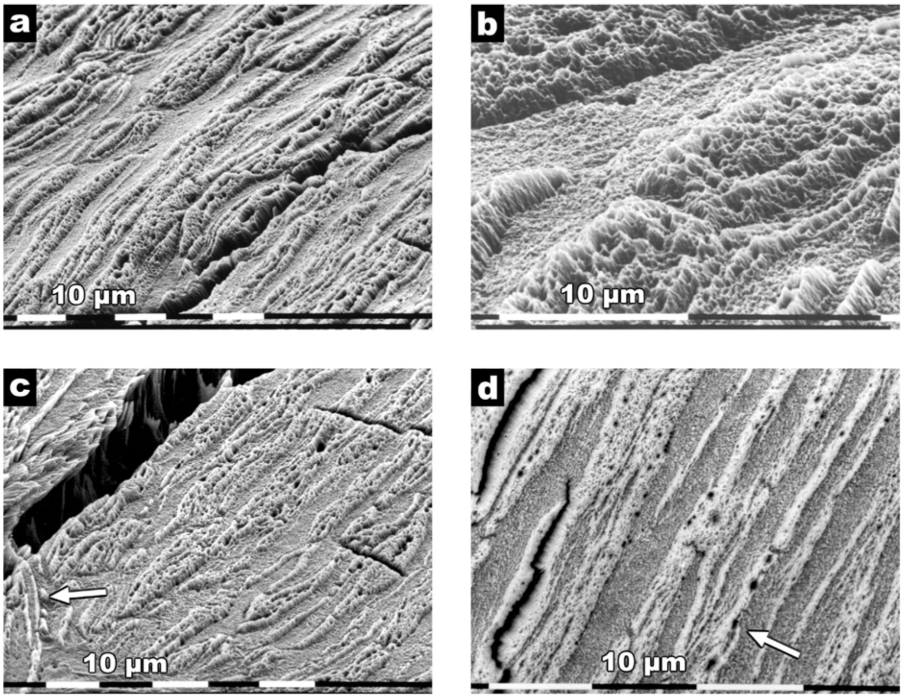

Fig. 2. Unidirectional compactions below the optimum, transverse sections (a) specimen B at 151.6 °C, tilted; (b) detail of similar region; (c) specimen C at 152.0 °C tilted; (d) flat-on.

Both etched specimens are seen to have undergone cracking, with the larger scale cracks being those which run along the tape width (oriented as in Fig. 1(b)). The smaller cracks which run across the thickness of the tapes are almost certainly a response only to the stresses imposed by the microtoming, whereas the ones along the width are in response to a combination of microtoming and incomplete consolidation of the ribbon-like units. The pattern in Fig. 2(d) especially suggests that the ribbon-like units are to be traced according to the distribution of the cratered and flatter components, with each unit having an interior of the flat component and the cratered component forming a skin of variable thickness. This interpretation is supported by the details in Fig. 2(d), firstly a line of small 'void-like' features indicated by the arrow, and secondly by the cracks at left, which mostly run down the middle of the cratered regions. This is also borne out by the arrowed feature in Fig. 2(c), which is a small group of misaligned ribbon which may have arisen during the initial fabrication of the tape or else have been displaced during the compaction process. On this basis one might consider that the fabrication of the tape comes from a bundle of fibres with a exterior resistant to etching like those in Dyneema® [6,9] which have been flattened together in some form of 'kneading' process, forming a flaky-pastry-like texture.

Longitudinal views reveal that the two morphological components also differ in their lateral etching rates. That of specimen B from the lowest compaction temperature, 151.6 °C, Fig. 3(a), has a linear structure with parallel raised ridges much more pronounced than that of the original tape (compare Fig. 1(c)) and a little evidence of intervening transcrystallinity. For specimen C the scale of texture seen in Fig. 3(b) matches that in the transverse view of Fig. 2(d) and reveals bands (arrowed A) of what look

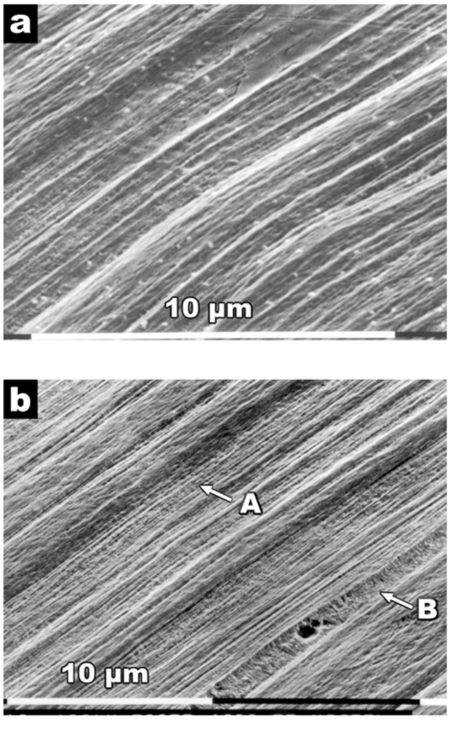

Fig. 3. Longitudinal sections of compactions below the optimum (a) specimen B; (b) specimen C showing different longitudinal appearances.

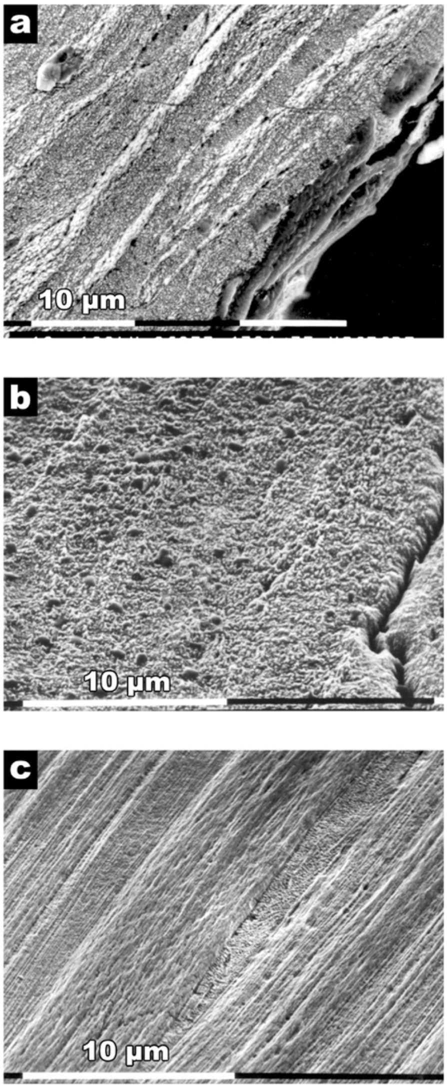

Fig. 4. Unidirectional Tensylon at the optimum compaction temperature 152.9 °C (specimen D) (a) transverse section, flat-on; (b) transverse section, tilted; (c) longitudinal section.

like 'fibrillar spines' which are somewhat spaced and with transcrystalline development in between, while the laddered texture (arrowed B) below centre is evidence of a junction of melt-crystallized material formed between two subunits [8]. The band running just below and to the right of this junction appears different to that on the other side, and quite different from the band arrowed A. This is not due to misalignment, and this type of variation is generally seen in this specimen and in specimen D (152.9 °C: the optimum temperature). The band below does not contain the long ridges, but is composed of shorter units. Such bands are raised slightly above the transcrystalline texture in the etched surface, and it is considered that this type of structure may be related to the raised cratered texture seen in transverse section, while the majority transcrystalline texture may relate to the more heavily etched material in the flat regions of the transverse section.

At the optimum compaction temperature of 152.9 °C, for specimen D, there is a distinct change in the morphology. While in transverse sections viewed flat-on as in Fig. 4(a), the two components are clearly visible, with differential contrast related to fine details of surface topography, tilting as in Fig. 4(b) shows that much of the coarse relief has disappeared with the cratered structure now only distinguishable on close inspection as a somewhat coarser texture although grooved boundaries between the ribbon-like subunits are still discernible. No voids are visible in these boundaries, which is consistent with the maximum transverse strength being attained at this compaction temperature. In longitudinal section, Fig. 4(c), the lateral scale of the surface ridging matches that of the transverse section and the distinction between the two types of structure is more evident.

At the highest compaction temperature studied, 154.1 °C, specimen E, the transverse structure is completely transformed although X-ray patterns suggest a substantial degree of remaining preferred molecular orientation [6]. Neither in flat-on view, Fig. 5(a), nor after tilting, Fig. 5(b), are major morphological features evident, only undulations and a fine pitting. However lines of tiny voids (lower right of picture) in some places may indicate the boundary between original subunits. Such lines of voids are similar to those seen in etched surfaces of consolidated UHMWPE in hip cups [10]. In longitudinal section of Fig. 5(c) is shown how the material retains well-oriented ridges whose length is, however, now reduced to a few micrometers; the transcrystalline detail is also more prominent.

3.3. Compactions—woven fibre

The use of woven cloths in two-dimensional compactions has previously been studied in Certran polyethylene [5,11] and in polypropylene [12–14]. In the polypropylenes and especially in the Certran PE, optimum compaction in terms of properties was achieved at temperatures where sufficient melt was produced to fill gaps between the compacting fibres [11] and tapes, this amount increasing when the respective geometries did not allow good packing between different elements. The problem alluded to in the previous study of compacted woven Certran fibres [11], was that there was only a very small window between the temperature needed to produce sufficient melt to bind the structure together and the onset of substantial crystalline melting and loss of orientation. In Tensylon compaction, the molecular network appears to persist even when substantial crystalline melting occurs and it seems that the tapes are able to deform more readily to fill the gaps completely. The low magnification view in Fig. 6(a) of a two-dimensional compaction at 153 °C, Specimen F, shows different tapes within the weave but no large voids or pools of recrystallized melt. In certain cases, notably where longitudinal and transverse fibres meet, Fig. 6(b), some voids are present as at the right of picture. In this picture the differential relief of the two

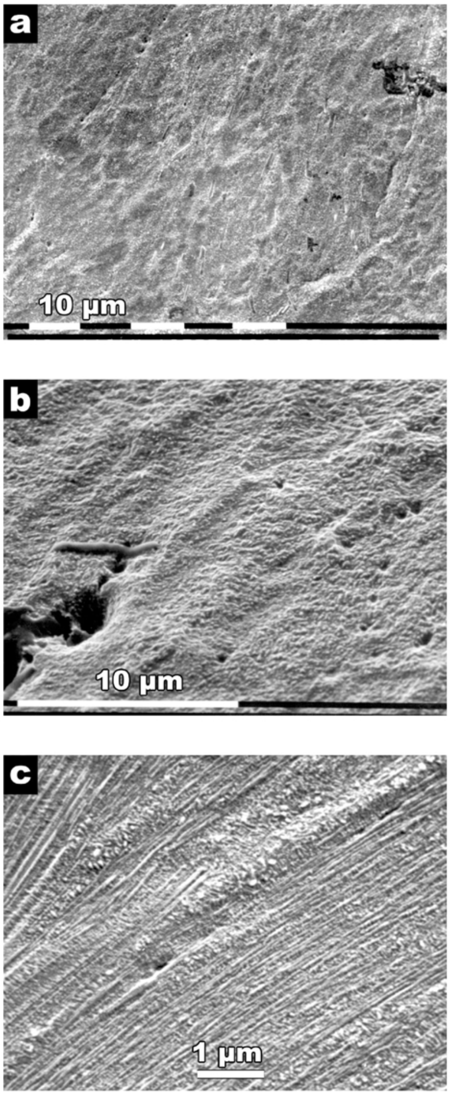

Fig. 5. Unidirectional Tensylon at 154.1 °C, above the optimum (specimen E) (a) transverse flat-on; (b) transverse tilted; (c) longitudinal direction.

morphologies in the transverse section is very clear. At the top of this figure the structure can be related to the subunits seen in the original material but at the bottom it appears to be have been considerably distorted. The raised cratered structure seen at higher magnification in Fig. 6(c) closely resembles that in cross-sections normal to the fibre in previous polyethylene compactions, particularly Certran and Spectra, but especially the rims of Dyneema fibres, while the lower lying regions in between are like the lower central parts of those same fibres. The corresponding morphology in longitudinal section Fig. 6(d) shows ridges—now revealed to be sheets or walls normal to the page [15]—of varying heights. Where there are many parallel ridges these have transcrystalline connections, otherwise the intervening areas are fine-grained but less well organized. These again may be attributed to the two components which give rise to the lower lying and cratered displayed in transverse section.

4. Discussion

The developing morphologies with increasing compaction temperature place Tensylon more with Spectra and other gel-spun fibres rather than with Certran, where the greatest melting takes place between 140 and 143 °C, outwards from the linear density deficient regions with high free volume which are present in all the materials during their manufacture. This leads to the etched craters having flat floors displaying the basal surfaces of recrystallized lamellae [16]. In all the other higher melting materials the polymer melts internally and progressively within a network of high-melting walls. The most thoroughly studied of these materials is the melt-kneaded Tekmilon [15] whose behaviour, in common with other similar materials, points to the existence within it of a highly extended entangled molecular network as indirectly confirmed by its high melting point under constraint after formation of the hexagonal phase [17,18]. The gel-spun fibres (Dyneema, Spectra) were also found to display similar behaviour [19,20]. In all of these cases, the DSC melting endotherm, whether of a constrained fibre or a compaction, shows a small final peak, since the main 'melting' peak includes some material undergoing the orthorhombic-to-hexagonal transition, with a corresponding smaller hexagonal-melt peak immediately following [6,15]. All of these fibres developed a 'spine and transcrystalline' morphology when partially melted under constraint when tied around a copper spool in the DSC, though the 'spines' are in fact more like ribbons or walls. In transverse section they showed similar small protruding features seen in the tilted view, which may possibly be portions of the network that have consolidated while the system is mobile.

Another feature of Certran is that during compaction a significant quantity of melt is exuded outside the fibre. For this reason it behaves differently in unidirectional compactions and woven fabrics. In the former, at the optimum temperature only 8% of the original fibre melts [8], but this is sufficient to fill the gaps between the circular fibres without their being subjected to much distortion. In the woven structures, the optimum temperature is ~1.5 K higher, so that nearly 30% of melt forms, sufficient to fill the much larger gaps found in the woven cloth. Here with Tensylon the optimum temperature for both unidirectional and woven compactions is found where between 60 and 70% of the original oriented crystal remains after compaction: however, very little of the molten material escapes from either the whole tapes or their subunits to form crystalline junctions such as that seen in Fig. 2(d). In Dyneema this is to be expected since this fibre has a skin which is more resistant to etching [9] and higher melting than the bulk of the fibre; moreover the individual fibres are greatly distorted during compaction. While Tensylon appears to be somewhat similar in that the skin of the subunits is more resistant to etching, its geometry, both in terms of the tapes and the ribbon-like sub units, is more conducive to easy packing

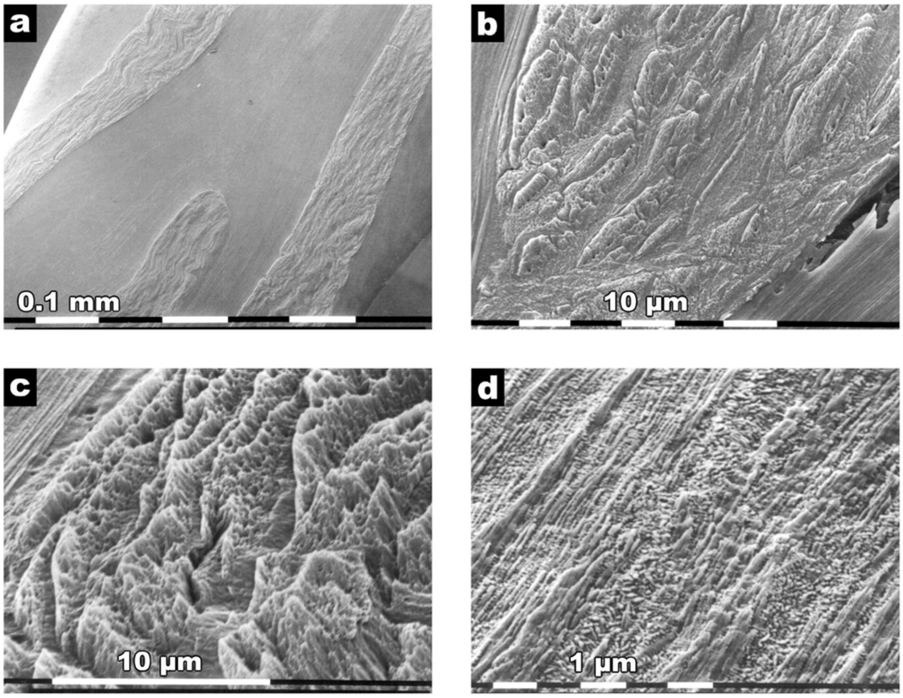

Fig. 6. Specimen F, compacted weave (a) low magnification; (b) transverse and longitudinal morphologies; (c) detail of transverse morphology; (d) detail of longitudinal morphology.

than the bean-shaped cross-sections of Dyneema. The gel-spinning process is designed to reduce entanglements to the point where the high degree of orientation and modulus development is possible, but leaving sufficient of them to provide the network which the integrity of the fibre depends on. Although Tensylon is produced by a very different process, the same effect appears to have been achieved. The importance for compaction is that the entanglements in this network act like transient cross-links, with a half-life of perhaps several minutes. They thereby constrain the stretched-out molecular segments so they cannot immediately relax into something approaching a random coil, consequently the entropy of the melt phase as it forms is reduced and allows the network to form a higher melting population which survives the compaction treatment. What appears to give the advantage to Tensylon, with its slightly broader processing window, is the favourable geometry of the fibres with an increased surface area to volume ratio.

5. Conclusions

In this paper we have examined the development of morphology during the hot compaction of Tensylon polyethylene tapes. In general, the Tensylon tapes are made up of ribbon-like units which show a two-component morphology both before and after hot compaction. After etching this appears as cratered ribbons emerging from a flat, relatively featureless landscape, probably reflecting a stage in the fabrication history. Interestingly, this morphological distinction disappears at the optimum compaction temperature (~153 °C) at the point where the best combination of mechanical properties were observed in a previous publication [6]. Morphological comparison with other polyethylenes and their compacted samples places Tensylon behaviour alongside Dyneema, Spectra and Tekmilon rather than the melt-spun Certran. This is related to the molecular entanglement network, but here it is combined with the ribbon-like geometry of both the tape and its subunits to give a wider useful temperature window for processing.

References

[1] Capiati NJ, Porter RS. The concept of one polymer composites modelled with high density polyethylene. J Mater Sci 1975;10:1671–7.

[2] Hine PJ, Ward IM, Olley RH, Bassett DC. The hot compaction of high modulus melt spun polyethylene fibres. J Mater Sci 1993;28:316–24.

[3] Hine PJ, Bonner MJ, Brew B, Ward IM. Hot compacted polypropylene sheet. Plast Rubber Compos Process Appl 1998;27:167–71.

[4] Rasburn J, Hine PJ, Ward IM, Olley RH, Bassett DC, Kabeel MA. The hot compaction of polyethylene terephthalate. J Mater Sci 1995;30:615–22.

[5] Bonner MJ, Hine PJ, Ward IM. Hot compaction of crosslinked high modulus polyethylene fibres and fabrics. Plast Rubber Compos Process Appl 1998;27:58–64.

[6] Hine PJ, Ward IM, Jordan ND, Olley RH, Bassett DC. A comparison of the hot-compaction behavior of oriented, high-modulus, polyethylene fibers and tapes. J Macromol Sci Phys 2001;40(959):989.

[7] Shahin MM, Olley RH, Blissett MJ. Refinement of etching techniques to reveal lamellar profiles in polyethylene banded spherulites. J Polym Sci, Polym Part B: Polym Phys 1999;37:2279–86.

[8] Olley RH, Bassett DC, Hine PJ, Ward IM. Morphology of compacted polyethylene fibres. J Mater Sci 1993;28:1107–12.

[9] Abo El Maaty MI, Olley RH, Bassett DC. On the internal morphologies of high-modulus polyethylene and polypropylene fibres. J Mater Sci 1999;34:1975–89.

[10] Olley RH, Hosier IL, Bassett DC, Smith NG. On morphology of consolidated UHMWPE resin in hip cups. Biomaterials 1999;20:2037–46.

[11] Hine PJ, Ward IM, El Maaty MIA, Olley RH, Bassett DC. The hot compaction of 2-dimensional woven melt spun high modulus polyethylene fibres. J Mater Sci 2000;35:5091–9.

[12] Hine PJ, Ward IM, Teckoe J. The hot compaction of woven polypropylene tapes. J Mater Sci 1998;33:2725–33.

[13] Teckoe J, Olley RH, Bassett DC, Hine PJ, Ward IM. The morphology of woven polypropylene tapes compacted at temperatures above and below the optimum. J Mater Sci 1999;34:2065–73.

[14] Amornsakchai T, Bassett DC, Olley RH, Hine PJ, Ward IM. On morphologies developed during two-dimensional compaction of woven polypropylene tapes. J Appl Polym Sci 2000;78:787–93.

[15] Teckoe J, Bassett DC, Olley RH. Aspects of the morphology and melting behavior of constrained polyethylene fibers. Polym J 1999;31:765–71.

[16] Kabeel MA, Bassett DC, Olley RH, Hine PJ, Ward IM. Differential melting in compacted high-modulus melt-spun polyethylene fibres. J Mater Sci 1995;30:601–6.

[17] Tsubakihara S, Yasuniwa M. Melting and crystallization of ultra-high molecular weight polyethylene with appearance of hexagonal phase. II. Strain-induced crystallization of thermal-contracted sample. Polym J 1996;28:563–7.

[18] Tsubakihara S, Nakamura A, Yasuniwa M. Melting and crystallization of ultra-high molecular weight polyethylene with appearance of hexagonal phase. I. Melting processes of fibers under constrained state. Polym J 1996;28:489–95.

[19] Teckoe J. PhD Thesis. University of Reading; 1998.

[20] Yan RJ, Hine PJ, Ward IM, Olley RH, Bassett DC. The hot compaction of SPECTRA gel-spun polyethylene fibre. J Mater Sci 1997;32:4821–32.