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The hot compaction of polyethylene terephthalate

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A process is described for the successful compaction of polyethylene terephthalate fibres. The measurement of mechanical properties shows that a very high proportion of the original fibre properties are retained and that the compacted samples have a good degree of coherence. Electron microscopy studies of suitably etched samples reveals the effect of the compaction temperature on the structure of the compacted samples.

1. Introduction

The successful compaction of ultra-high modulus melt-spun polyethylene fibres, at temperatures within the melting range, yet with the retention of many of the properties of the original fibre, has been reported previously [1, 2]. Materials of large cross-section, good cohesion and high stiffness result from this ostensibly simple process. The method capitalizes on the intrinsically favourable melting characteristics of the fibres, so that only a small fraction is melted, and no second component, such as a thermosetting resin or added low-molecular-weight polyethylene, is required. Moreover, it appears that the more influential parameter is the choice of temperature for this process, rather than the applied consolidating pressure, for ensuring a coherent material. Apart from the obvious technological interest in this technique, compacted materials can also serve as platforms in which the internal structure of the constituent fibres can be examined by, for instance, electron microscopy.

Structural analysis [1, 2] of the compacted melt-spun polyethylene material reveals a composite structure consisting of fibrous material embedded in recrystallized polymer, the latter having been produced by the melting of the outermost regions of the individual fibres such that they revert to the lamellar state. TEM analysis reveals the prominent self-nucleation on the fibres, leading to the development of transcrystalline lamellae with *c*-axes parallel to that of the fibres on which they grow [2]. Such good interfibrillar connection together with the common orientation leads to moduli, in the fibre direction, comparable with the original fibre itself.

Electron microscopy also revealed that the onset of melting was strongly influenced by physical factors, specifically the availability of free volume, not only at the outer surface but also in long internal regions parallel to the fibre length. Such behaviour helps improve intrafibrillar cohesion and also gives insight into the mechanisms underlying successful compaction.

In this paper, the effectiveness of the compaction method for polyethylene terephthalate (PET) fibres is demonstrated, illustrating again the key role played by the temperature employed. Electron microscopy again highlights many of the features previously found in the polyethylene compactions, but in some cases, such as the degree of coalescence of adjacent fibres, more conspicuously.

2. Experimental procedure

The PET fibre (ICI plc) used was typical tyre cord yarn, having the properties shown in Table I. The linear density of the yarn was 1000 denier (1100 decitex), containing nominally 96 filaments per fibre tow, with a filament diameter of ~ 15 μm.

2.1. Sample preparation

A specimen of fibre was wound unidirectionally using specialized winding apparatus and then placed between matching mould plates, having a contact surface area of 55×55 mm^2. The assembly of fibres and mould was then placed in a hot compression press, this being pre-set so as to give the required compaction temperature. A suitable value for the compaction temperature was assessed from the melting endotherm of the original fibre, determined by differential scanning calorimetry (DSC): in general, a temperature within the melting range was selected. The temperature was monitored by a thermocouple probe inserted in the upper mould plate. With the sample in the press, a pressure of 1.85 MPa was applied (270 p.s.i.) to prevent the shrinkage of the fibres during heating. At the end of 15 min, a pressure of 32.4 MPa (0.32 k bar, 4800 p.s.i.) was applied to consolidate the compaction. Immediately afterwards, the temperature setting was reduced to 200 °C, and once the mould had reached this temperature it was removed from the press and allowed to cool in air.

TABLE I

Grade	Modulus (GPa)	Density (g cm^{-3})
38035T800	15	1.39

2.2. Differential scanning calorimetry

Thermal analysis of the original fibres and the compacted materials was carried out on a Perkin–Elmer DSC-7 series differential scanning calorimeter, in a nitrogen atmosphere, up to temperatures of 320 °C. The scanning rate for all the tests was 10 °C min^{-1}.

2.3. Mechanical analysis

The mechanical performance of the compactions at room temperature was assessed from their flexural moduli and flexural strength in standard three-point bend tests using an Instron testing machine. A cross-head speed of 1 mm min^{-1}, bridge span of 40 mm and specimen width of 10 mm were used. Following the ASTM recommendations [3], thin specimens, of typical thickness 1.2 mm, were used for modulus determinations and thick specimens, of typical thickness 2.4 mm and incorporating more fibre during fabrication, were used to determine the flexural strength. The properties longitudinally, i.e. parallel to the fibre direction, and transversely, i.e. perpendicular to the fibre direction, were obtained from specimens machined in the appropriate directions.

The original fibres were tested in tension on the Instron machine using a gauge length of 200 mm and cross-head speed of 1 mm min^{-1}, to give the same specimen strain-rate as used in bending (10^{-4} s^{-1}).

2.4. Electron microscopy

The PET compactions were examined in transverse and longitudinal sections. Initially, specimens were cut with a diamond knife both across and along the fibre direction, as for the polyethylene composites already reported [1, 2, 4]. However, this produced periodic damage or chatter, particularly in the longitudinal sections, which was grossly aggravated by etching. Therefore, samples for etching were mounted in a block of L. R. White resin, and surfaces ground and polished with successively finer grades of alumina powder.

Cut surfaces were examined optically under reflection in Normarski Differential Interference Contrast, while ground surfaces were etched, gold coated and examined under a Philips 515 Scanning Electron Microscope. Two alternative etching procedures were used, as described in the text.

A 21% solution of sodium ethoxide in ethanol for 2.75 h (Reagent 1) gives stronger etching in contrast to less severe results from samples immersed for 19 h in a mixture of 2 g potassium hydroxide, 2.1 g water, 16.6 g iso-amyl alcohol, 1 g cetyl trimethyl ammonium bromide and 3.7 g Triton X-100 (Reagent 2).

3. Results and discussion

3.1. Sample appearance

As was found in the previous compaction studies on polyethylene fibres, successful compaction required temperatures within the melting range of the PET fibres, which for this fibre was between approximately 250 and 262 °C. This is, however, a much wider available temperature range than the polyethylene fibres previously studied. Compactions at temperatures below 250 °C resulted in weak and incohesive materials. Within the melting range of the fibres, however, strong and stiff plaques were obtained in which little of the fibrous nature of the starting material could be discerned by eye.

3.2. DSC measurements

All the compactions reported in the present study were made at temperatures in the leading (low-temperature) side of the melting peak of the basic fibre (i.e. below 257 °C, Fig. 1); at higher temperatures, the fibres melted completely and the sample was ejected from the mould.

Two features revealed in Fig. 1 contrast with previous experience for melt-spun polyethylene fibres. Firstly, the compacted materials have a notably higher temperature for the onset and peak of melting than the original, unconstrained fibre. This is in accord with earlier observations of raised melting points [5] when PET fibres are held at constant length arising from the reduction in entropy of an oriented, as opposed to a random, melt. The same physical explanation was advanced, especially in relation to differential melting phenomena, in our studies of compacted polyethylene fibres [2, 3]. The effect is demonstrated in Fig. 2, for a tightly knotted specimen of the original fibre, whose peak melting point was 10 °C higher than when unrestrained: the constrained melting peak was also substantially larger than the unrestrained one.

In both polyethylene and PET compactions, the constraint on any one fibre will arise through the influence of its neighbours. The amount by which the melting point is raised will depend upon the precise constraint of the molecular network in the sample in relation to the thermodynamics of the system. Although this is a matter of great interest, it is beyond the scope of the present paper.

The melting point of compacted fibres is also liable to rise, as it did in polyethylene [1], because of increases in crystal thickness brought about by annealing, i.e. heating to and holding at the compaction temperature [5–8]. Fig. 3 shows the effect for an unconstrained fibre, annealed within the melting range for 3 min then cooled at 20 °C min^{-1} before its endotherm was recorded; the endotherm of a specimen compacted at 254 °C is included in Fig. 3 for comparison. For the annealed fibre, the main melting peak has shifted up by about 4 °C and there is also evidence of a lower melting peak: the compacted sample endotherm shows similar features to the annealed sample. Fig. 4 shows how the peak melting point increases through the range of compaction temperatures. In general, annealing tends to increase the

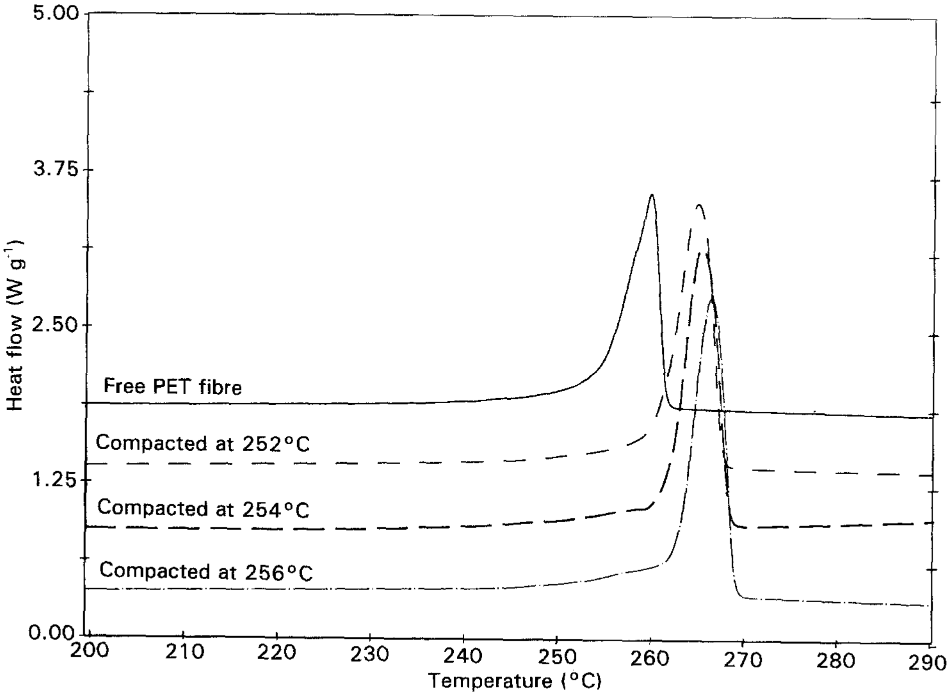

Figure 1 DSC melting endotherms for PET compactions (252, 254 and 256 °C) compared with the free PET fibre.

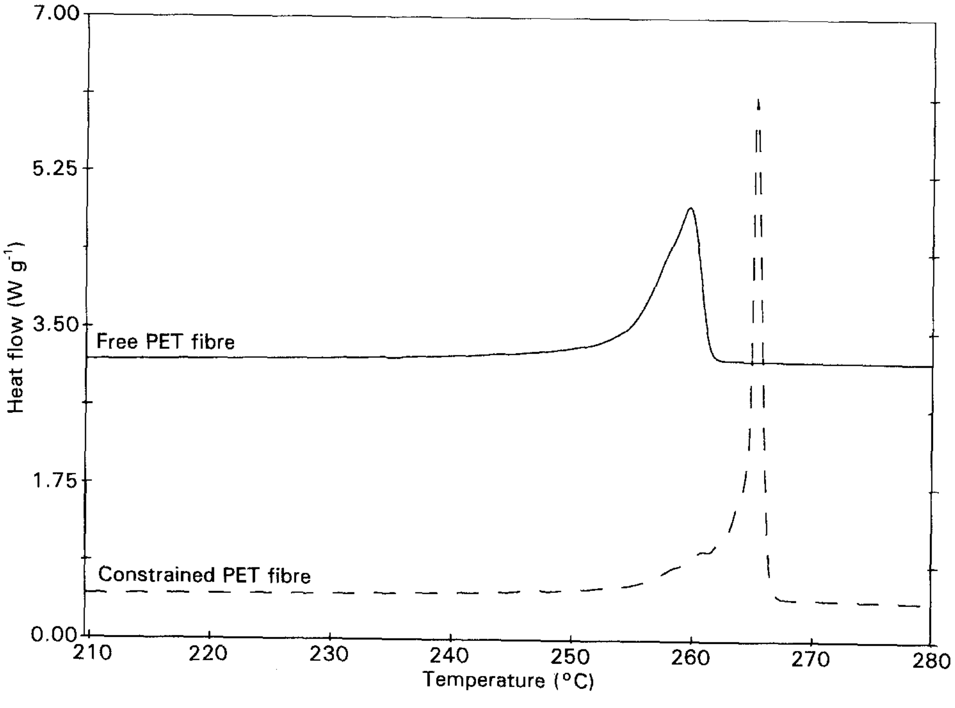

Figure 2 DSC melting endotherms for free and constrained PET fibre.

enthalpy of fusion possibly due in part to increased crystal thickness but mostly to additional crystallinity generated in the process. There is, however, no evidence of any significant increase in crystallinity in our samples (Fig. 5).

The second point concerns the apparent absence in Fig. 1 of the additional low-temperature peak that was conspicuous in the polyethylene compactions and was attributed to the lamellar and non-fibrous component. We propose this is because the recrystallized PET has a similar melting point to the fibrillar crystalline regions, so that its endotherm is subsumed into that of the remaining fibre. Experimental support is provided as follows. When an unconstrained fibre is heated beyond its melting range, cooled at 200 °C min^{-1} and remelted at 10 °C min^{-1}, an endotherm as in Fig. 6 results. It can be seen that after the rapid cooling following the first heating, the recrystallized material does possess a similar melting range to the original fibre. However, a very faint suggestion of a lower melting peak is seen in the compaction at 256 °C, the lowest curve in Fig. 1. Presumably, this is attributable

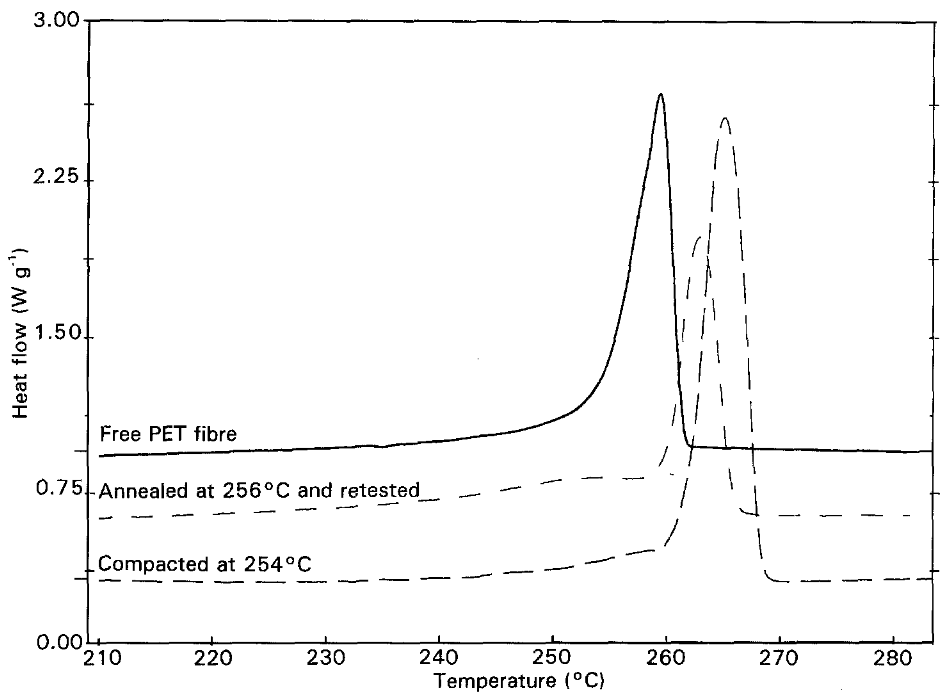

Figure 3 DSC melting endotherms showing the effect of annealing the original fibre.

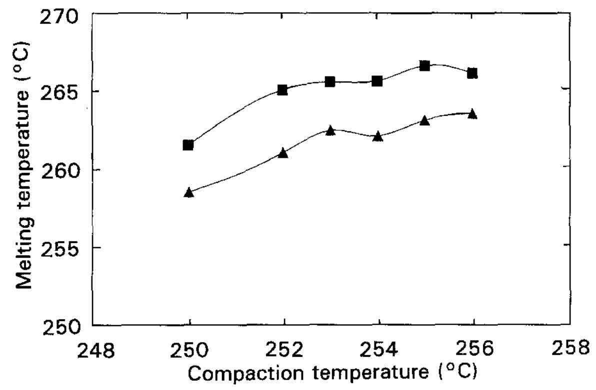

Figure 4 (▲) Onset and (■) peak temperatures for a range of compaction temperatures.

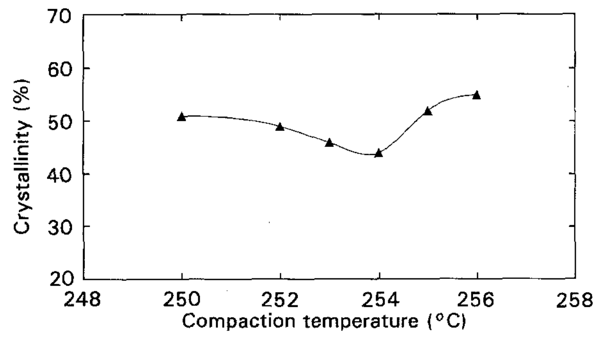

Figure 5 Crystallinity of compacted samples versus compaction temperature.

to a growing amount of recrystallized material while melting of the remaining fibre phase is shifted to higher temperatures as discussed above.

3.3. Mechanical performance

The longitudinal moduli (Fig. 7) of the compacted fibre samples again parallel the behaviour found with the melt-spun polyethylene fibres [1]. At low compaction temperatures the lower values, compared to the original fibre modulus, reflect incomplete compaction and the presence of lateral voids. A maximum in the modulus emerges at intermediate temperatures, when filling of voids by molten polymer has given a coherent material with a minimal amount of fibre having been melted in the process. The subsequent decline in the modulus with increasing compaction temperature is primarily due to a loss of orientation of the melted and recrystallized part of the sample.

The transverse modulus and strength (Figs 8 and 9) both increase steadily with the compaction temperature. Factors contributing to the former will be the improved continuity when lateral voids are filled together with the increasing fraction of chains oriented transversely which loss of axial orientation will provide. Concerning strength, there is much variation in measured strength values for any one particular compaction temperature, possibly because when tested at room temperature the material is below its glass transition and therefore very brittle and flaw-sensitive.

Unlike the polyethylene compactions which delaminated or yielded in a ductile manner when failing, these PET compactions failed in a sudden and brittle manner, usually with the specimen fracturing completely. In such circumstances, the role of imperfections leading to cracking would be expected to affect the measured strength of the specimen, and increase the variability more than was found with the polyethylene compactions. Nevertheless, the improvement with increasing compaction temperature is likely to be a consequence of improved continuity both within the fibres by elimination of defect and externally, by the

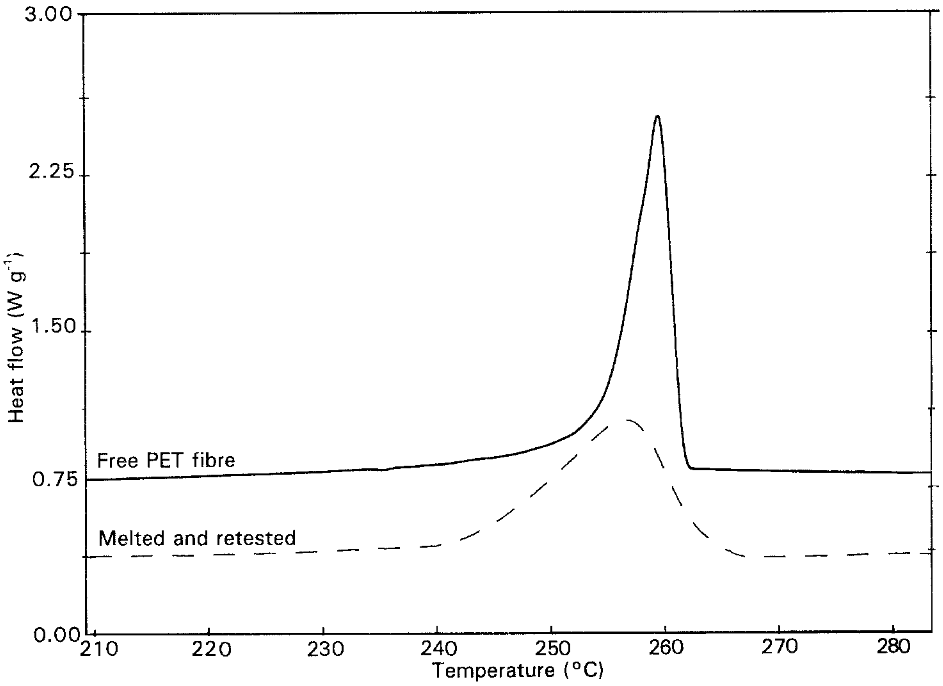

Figure 6 DSC melting endotherms showing the effect of completely melting the original fibre.

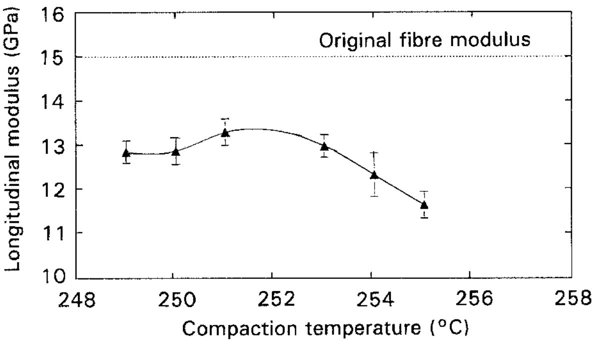

Figure 7 Longitudinal modulus versus compaction temperature.

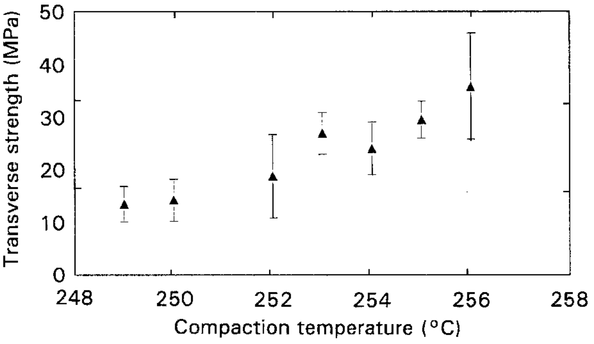

Figure 9 Transverse strength versus compaction temperature.

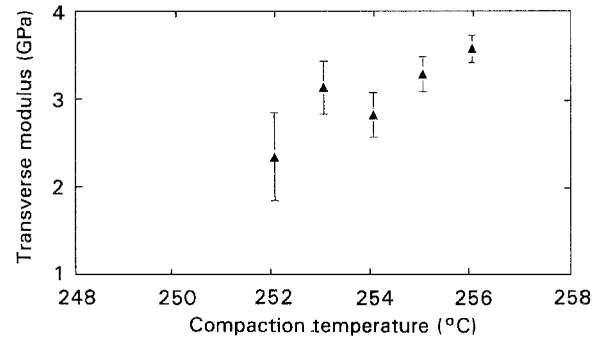

Figure 8 Transverse modulus versus compaction temperature.

development of epitaxial overgrowths with inherently strong connections.

3.4. Electron microscopy analysis

Transmission electron micrographs of two transverse sections from the PET compactions, etched as described in Section 2.4, are shown in Fig. 10. Compared to melt-spun polyethylene [1, 2, 4], the PET-recrystallized material is much more readily attacked by the etchants used than are the fibre cores. In consequence, during a period of etching which produces satisfactory clarity in the fibre detail, the intervening material is extensively eroded. It follows that such material is more penetrable by the etchant. This could simply be a consequence of a low-crystallinity system, but might also reflect reduced crystallographic or mechanical continuity.

The contrast between the lower (250 °C) and higher (255 °C) compaction temperatures, shown in Fig. 10a and b, respectively, is quite clear, with the fibres remaining very distinct in the former case whilst in the latter, the more extreme temperature conditions have succeeded in apparently causing fibres to coalesce. Fig. 11 shows transverse cross-sections, imaged by reflection using Nomarski interference contrast optics, of compacts cut open but not etched. Note the distinction between the shapes of the filamentary cross-sections: after compaction at 250 °C (Fig. 11a) they are mainly polygonal, owing to deformation during the final high pressure part of the preparation. Following

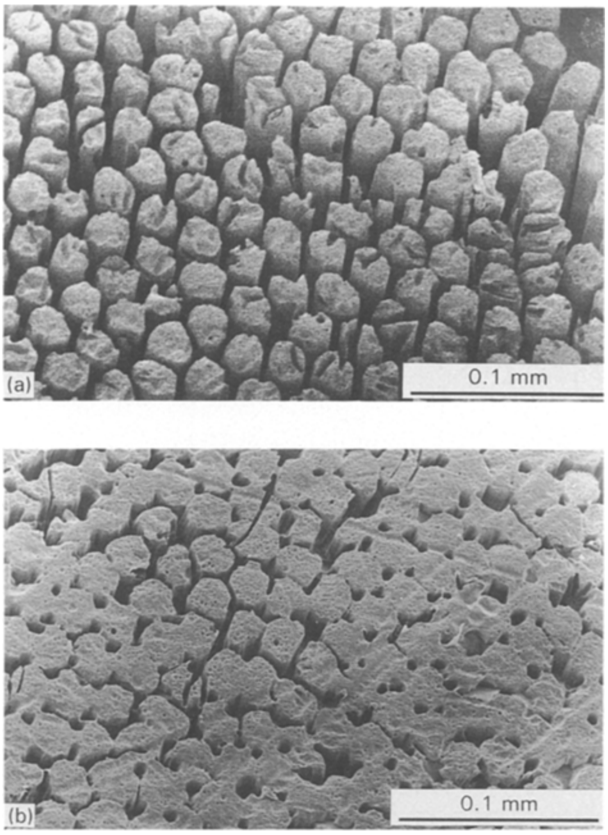

Figure 10 Etched transverse sections (TEM) for samples compacted at (a) 250 °C and (b) 255 °C (etched with Reagent 2).

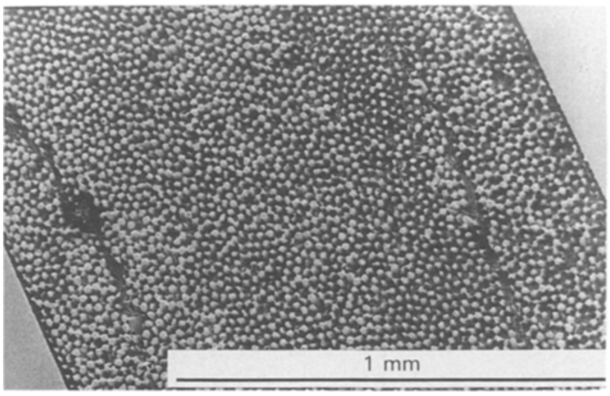

Figure 12 Etched transverse section of a sample compacted at 255 °C (etched with Reagent 1).

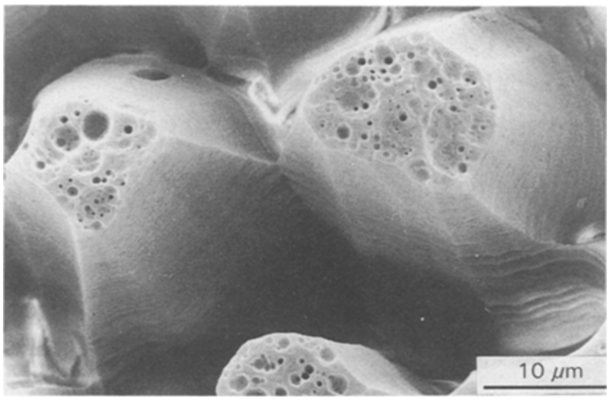

Figure 13 Etched transverse section showing fine detail of internal fibre structure (etched with Reagent 1).

treatment at 255 °C (Fig. 11b), the sections are more circular because of a more even distribution of pressure around the fibres arising from a larger amount of surrounding melt, which at the higher temperature would also be of a slightly lower viscosity. Moreover, the lateral spaces, which are often conspicuously empty at 250 °C, have been filled for compaction at 255 °C. Such behaviour is closely analogous to that found for melt-spun polyethylene.

In the transverse cross-section of a complete specimen as shown in Fig. 12, large areas can be seen at either side where there is almost no residual fibre but instead large gaps where the etchant has removed the melted and recrystallized polymer. By inference, these areas may be said to have been large pools of melt during compaction which, in turn, may have formed owing to gaps in the arrangement of the fibres or from the complete melting of filaments due, perhaps, to their being in a position of less restraint during compaction. To have been in a less restrained position, these fibres may have been slightly out of alignment during the preparation, or possibly not undergone as

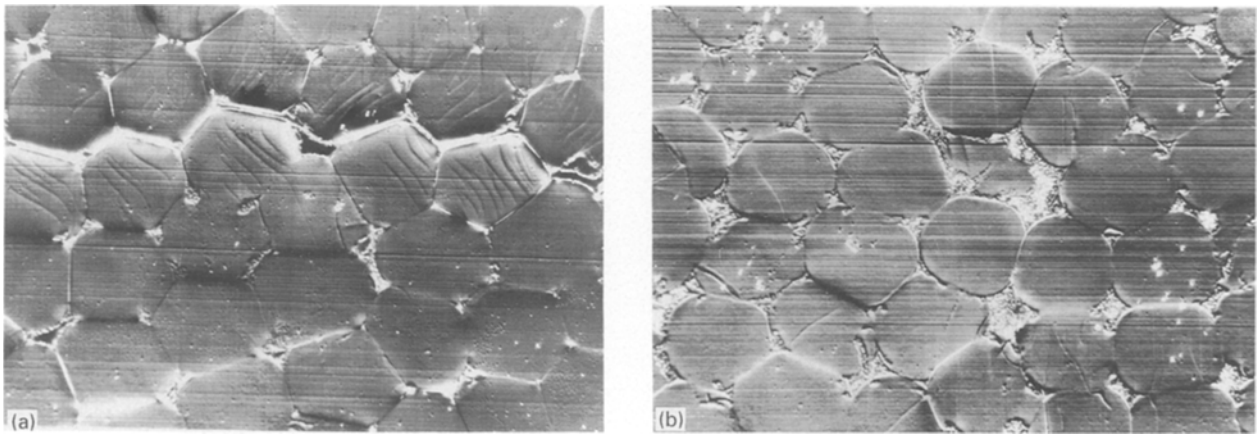

Figure 11 Cut but unetched transverse sections (viewed in reflected light) for samples compacted at (a) 250 °C and (b) 255 °C. Note that small variations in relief are brought about by differential relaxation of fibrous and non-fibrous components.

much orientation during drawing, unlike the majority. The large concentrations of recrystallized material that formed from these "pools" may be one explanation for the uncommonly high strength values that were found in some flexural tests.

Detail of the transverse sections of individual fibres, as in Fig. 13, reveals many holes where the etchant has progressed through lines of weakness within each fibre, as was seen first with the melt-spun polyethylene fibre and subsequently in other high-performance polyethylene fibres, then polypropylene and now PET. According to our previous discussion [9], the lines of weakness result from crystallization within a rigid framework with insufficient material available to fill the space at the ideal crystalline density. For these PET fibres the range of hole sizes is large with suggestions of grouping. The faceting on the outsides of the fibres is an artefact of the etching process, similar to that reported for polyethylene [2].

The longitudinal sections of Fig. 14 illustrate differing degrees of coherence at the filament boundaries. Where fibres have coalesced the boundaries are entire: elsewhere they have been generated by the etchant and large cavities excavated. The pleat structure on the fibres (Fig. 15) which can be seen at higher magnification and under more gentle etching, possibly represents a buckling phenomenon created during cooling, analogous to banded textures in liquid crystalline polymers [10].

3.5. Comparison with melt-spun UHM polyethylene fibres

It is interesting to enquire whether a general reduced relationship for compacted fibre material exists such that the relative decrease in longitudinal modulus with progressive melting is similar for many fibre types. This is the rationale for Fig. 16, in which the polyethylene and PET compactions are compared by normalizing the moduli by the respective values for the original fibres, and the abscissa compaction temperature as the fraction of the total melting temperature interval of the fibres, i.e.

Normalized temperature =

$$\frac{T_{\text{compaction}} - T_{\text{onset}}}{T_{\text{end of melting endotherm}} - T_{\text{onset}}} \quad (1)$$

where T_{onset} means the temperature at which melting commences. The agreement is gratifying given the difference in melting behaviour of the two fibres when under constraint.

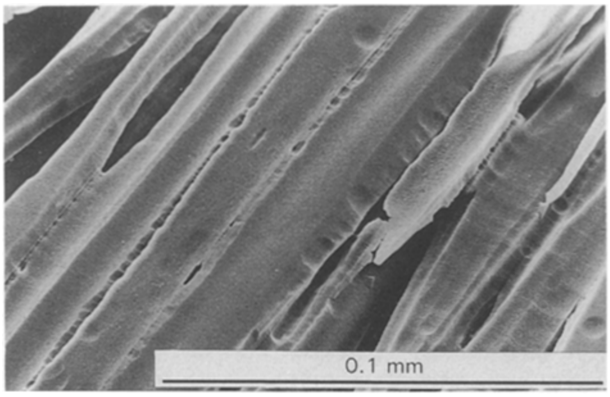

Figure 14 Etched longitudinal section for a sample compacted at 255 °C (etched with Reagent 1).

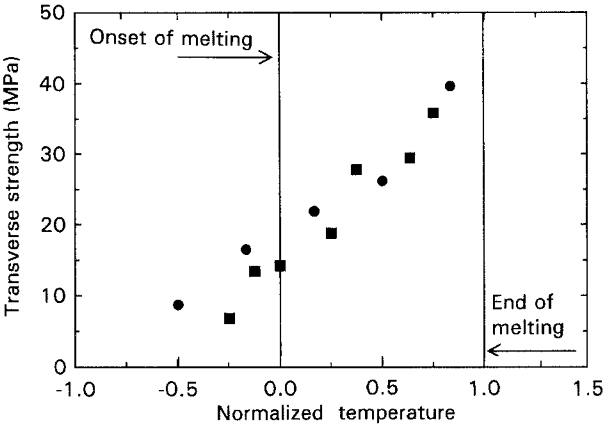

Figure 16 Normalized plot for longitudinal modulus versus compaction temperature, comparing (■) PET and (●) melt-spun polyethylene.

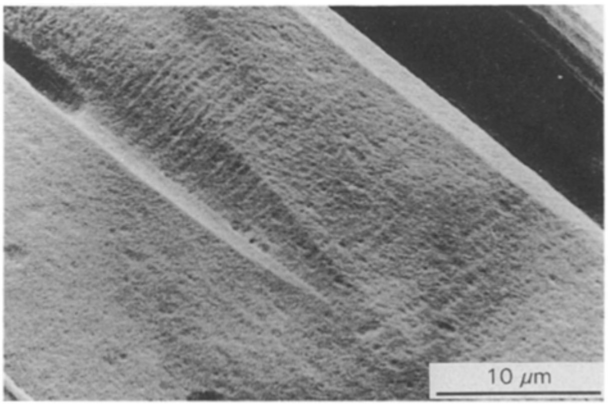

Figure 15 Etched longitudinal section for a sample compacted at 255 °C, showing fine detail of "pleat" structure (etched with Reagent 2).

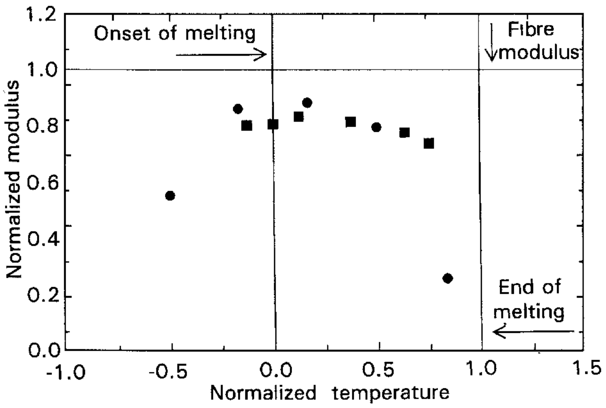

Figure 17 Normalized plot for transverse strength versus compaction temperature, comparing (■) PET and (●) melt-spun polyethylene.

The similarity in the transverse strengths (Fig. 17), plotted in a similar way, is more surprising, bearing in mind the different compositions, molecular weights, glass transition temperatures and molecular structure, and is possibly coincidental. Nevertheless, this plot is a helpful guide as to what constitutes a useful material. It appears that both types have finite strength when no melting has occurred ($x = 0$), but this may simply reflect the fact that a different heating rate is used in compaction and DSC experiments, with the consequence that the temperatures at which melting commences are not the same in each case. However, the application of high pressure, in the absence of any melting, may deform fibres so as to produce a degree of mechanical interlocking and so a measurable transverse strength.

4. Conclusion

It has been demonstrated that PET fibres of high modulus and strength can be successfully compacted, as was found in the case of UHM melt-spun polyethylene fibres. The important outcome is that a high percentage of the original fibre modulus is retained, yet with transverse strengths which are sufficient for useful applications. Both these properties reflect the good interconnection between fibres, which according to differential scanning calorimetry, are held in a position of constraint once compacted. Electron microscopy suggests, nevertheless, that good interfibrillar bonding is more difficult to achieve than was the case for melt-spun polyethylene fibres.

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