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Feature Article

The science and technology of hot compaction

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Abstract

The production and properties of single polymer composites is described, where the fibre and matrix phases are of identical chemical composition. The structure of the composites has been explored using mechanical tests, DSC and electron microscopy. Measurements of mechanical anisotropy, thermal expansion and impact behaviour are of especial interest.

The commercialisation of the hot compacted materials is also described. Potential applications include the automotive industry, sports protection goods, loudspeaker cones and helicopter radomes.

Keywords: Hot compaction; Oriented Polymers; Electron microscopy

1. Introduction

In this review article we describe the results of a research programme, which was initiated in 1989 as a research project at Leeds University within the IRC in Polymer Science and Technology. The initial aim was to explore whether composite structures could be produced from oriented thermoplastic fibres without the incorporation of a resin. The production of 'single polymer' composites from polyethylene fibres and polyethylene polymer had been shown previously by Porter and colleagues [1] but the aim of the new research was to achieve this by pressure and temperature only on an assembly of oriented fibres. This is the essence of the hot compaction method which has been shown to be widely applicable to a range of semi-crystalline and amorphous polymers.

The initial research was undertaken on high modulus melt spun polyethylene fibres, primarily for the reasons that the structure and properties of these fibres had been studied at Leeds since their discovery in the early 70s [2]. A further reason was that these fibres did have high stiffness and strength so that it was hoped that the compacted structures might have exceptionally high energy absorbing characteristics. This expectation was realised and, as will be seen, in fact exceeded by other oriented polymers, notably compacted polypropylene tapes.

The development of research on hot compaction is summarised in Table 1, which illustrates the various stages from 1990 to till date. During the first years, the possibility of hot compaction was explored for a wide range of fibres, including polypropylene, polyethylene terephthalate, gel spun fibres and thermotropic liquid crystalline fibres. The scientific understanding was crucially advanced by collaboration with Professor David Bassett and his colleagues at Reading University, especially Robert Olley, and their remarkable electron micrographs have done much to elucidate the effects of processing conditions on the physical properties, which have been studied in detail at Leeds. In addition to the scientific results, this first phase provided a significant patent portfolio, organised and funded by BTG.

By 1994 it was clear that the hot compaction technology could have significant commercial applications. A small incubation company was set up, VANTAGE POLYMERS, under the auspices of Leeds University, with Professor I.M. Ward as Chief Executive, Mr Derek Riley as Marketing Director and members of the initial research team including Dr Peter Hine and Mr Keith Norris. Initial funding for VANTAGE came from Hoechst Celanese but this led to a consortium of companies, with sponsorship from the FORD MOTOR COMPANY and valuable membership from AMOCO FABRICS and BI COMPOSITES. At the same time, the research base was widened to include manufacture

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Table 1
The timeline of the development of the hot compaction technology

Date	Event	Major funding body/institution
1990–1991	Initial Discovery	IRC Project 1990–1997
1992–1995	Inventions extended to many oriented fibres	IRC and BTG funding
1995–2000	Vantage Polymers	Initially a joint development project with Hoechst Celanese
2000–2003	Full scale commercialisation by BP	
1999–2003	Parallel scientific studies	EPSRC grants, BTG funding and BP funding

of sheets, postforming to produce real parts and detailed measurements of properties, especially for hot compacted polypropylene, which showed the greatest commercial potential.

By 2000, the commercial operations were sufficiently advanced to be transferred to BP AMOCO and research has continued at Leeds with support from EPSRC, BP AMOCO and BTG. This review article is primarily concerned with the scientific developments between 1990 and 2003, but mention will also be made of key commercial issues.

2. The hot compaction process—early studies on melt spun polyethylene fibres

The aim of the original research was to develop a technique for the production of novel composites where both the reinforcement and the matrix phases were polymeric, and moreover an identical polymeric material. The essence of the hot compaction process, developed at Leeds University, is to heat an array of oriented polymer fibres or tapes to a temperature where a thin skin of material on the surface of each fibre or tape is melted. On cooling this material recrystallises to form the matrix of a self-reinforced composite. This method of producing the ‘matrix’ phase of the single polymer composite, by selectively melting the surface of the oriented reinforcing phase, is the aspect of the hot compaction process which differs from the majority of the other studies which have been reported in the literature, where a second polymer is generally introduced to form the matrix phase. Techniques described [3–7] include film stacking, powder impregnation solvent impregnation and in the case of Cohen and co-workers [8], the use of pressure to control melting. A recent technique reported for producing single polymer polypropylene composites is the work of Loos et al. [9], where a bicomponent tape is used. Here the oriented tape is surrounded by a different low melting point polymer and on processing the outer skin is melted to form the matrix phase.

For the hot compaction process described in this review, it is felt that the virtue of melting the surface of the oriented phase is that the matrix is produced where it is needed, i.e. coating each oriented filament, and that the matrix is exactly the same material as the oriented phase. We believe that producing the matrix phase in this way creates molecular continuity between the original oriented fibre phase and the matrix phase (which as we will see epitaxially crystallizes onto the backbone of the oriented filaments), which gives a very strong bond between the two phases. This is confirmed by post examination of fracture surfaces from compacted sheets, where it is seen that the fracture often proceeds through the oriented fibres rather than at the interface between the matrix and oriented fibres [10].

The first studies were undertaken by arranging high modulus melt spun polyethylene fibres unidirectionally in a matched metal mould which was placed in a heated compression press. A small contact pressure (100 psi) was applied and maintained while the press temperature was raised into the region of the fibre melting point. A higher pressure (3000 psi) was then applied for a few seconds before removing the mould from the press and allowing it to cool to ambient temperature. The polyethylene fibres in these initial experiments were manufactured by Snia Fibre, Italy with the trade name of TENFOR, under a licence for the Leeds inventions (Capaccio and Ward) negotiated by the UK British Technology Group (BTG).

The very first compaction experiments were performed at temperatures below the melting point of the fibres. It was found that when the compaction temperature was increased into the melting range, the compacted sheets showed a transition from white to translucent in colour and a marked improvement in lateral strength with only a minor reduction in longitudinal stiffness and strength. The clearest indication of the nature of the successful hot compaction process comes from a combination of mechanical measurements and structural studies, including WAXS, DSC [10] and electron microscopy [11,12] of permanganate etched samples. The electron microscopy was undertaken by Professor David Bassett and his colleagues at Reading University in a very fruitful collaboration with the team at Leeds University, over a period of more than ten years.

DSC measurements on hot compacted samples normally show two melting endotherms (for example Fig. 1 which shows a CERTRAN melt spun PE sample compacted at 138 °C), one corresponding to the unmelted original fibre phase and a second low melting endotherm due to the polymer on the fibre surfaces which has melted and recrystallised. By careful control of the compaction temperature it is possible to adjust the proportion of the selective surface melting of the original oriented phase and so alter the fraction of the two phases. Fig. 2 shows a number of partial melting runs carried out in a controlled

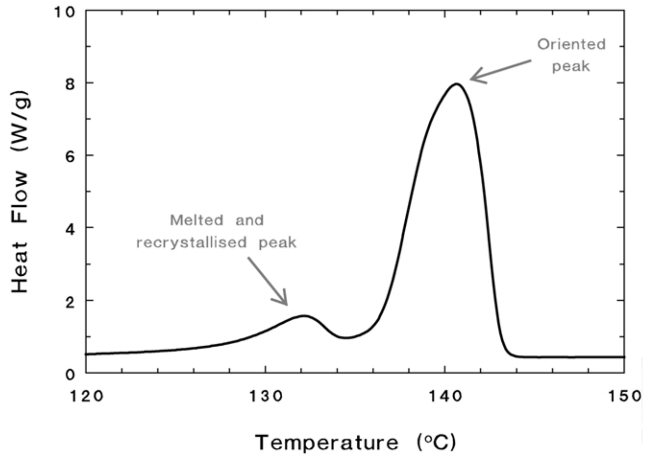

Fig. 1. DSC melting endotherm for a compacted CERTRAN melt spun polyethylene sheet made at 138 °C.

manner in a DSC [13]. Here a constrained unidirectional arrangement of CERTRAN PE fibres was taken to a set temperature (to represent a compaction experiment), held there for 2 min, cooled and then rescanned at the usual rate of 10 °C/min. The results show that the ratio of the two phases can be controlled if suitable temperature control can be achieved.

Measurements of the density, longitudinal flexural modulus and transverse flexural modulus versus compaction temperature show that there is an optimum processing window for the compaction process. Fig. 3 shows the longitudinal flexural modulus (measured parallel to the fibre direction) and transverse flexural strength of unidirectional samples of unidirectionally arranged CERTRAN melt spun PE fibres [10]. In the temperature range 136–140 °C the consolidation of the structure is complete so the density and longitudinal modulus reach their peak values and the transverse strength has risen appreciably. In practical applications it is best to use a woven fabric so that the transverse strength of the unidirectional fibre sheet is not of direct relevance and the peel strength of the hot compacted sheets, that is the force required to peel apart two woven layers, becomes the important parameter.

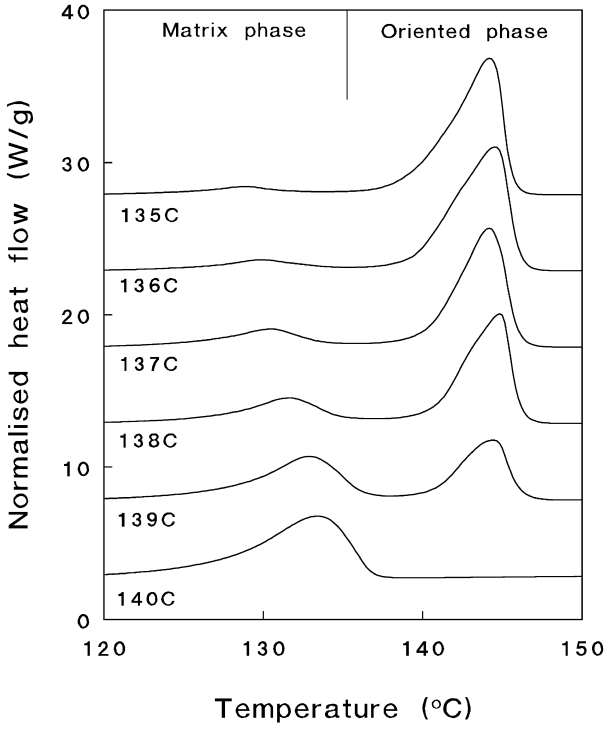

Fig. 2. Partial melting studies in the DSC showing the effect of compaction temperature on the percentage of the oriented and recrystallised matrix phases for CERTRAN melt spun PE.

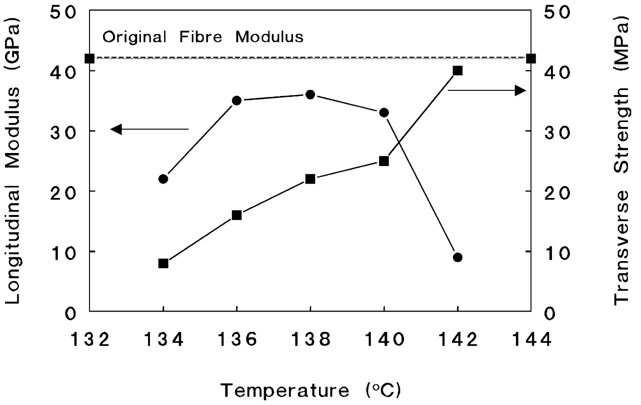

Fig. 3. Longitudinal modulus and transverse strength for unidirectional samples of CERTRAN melt spun PE fibres.

Scanning electron microscopy pictures (SEM) of etched compacted samples show how the recrystallised material neatly fills the interstices in the close packed, almost hexagonal array of fibres. Fig. 4a [14] shows a transverse section through a sample compacted at a temperature where around 25% of the oriented phase has been melted: (this sample would show a DSC trace similar to that of the partial melted sample made at 138 °C in the DSC on Fig. 2). While for a unidirectional arrangement of fibres only 10% melted material is required to fill the gaps in the structure and form a consolidated structure, in general a higher proportion of melted material is required to give good bonding between the fibres. Even more revealing are the etched longitudinal sections which show how the melted skins recrystallised epitaxially on the surfaces of the unmelted portion of the fibres, for example Fig. 4b [10]. Remarkably the polyethylene chain axis, the *c*-axis, in the lamellae of the recrystallised material, is parallel in every case to the fibre axis of the original fibres.

Even at this early stage of compaction of unidirectional polyethylene fibres it was recognised that the behaviour of the compacted material could be understood in very reasonable quantitative terms on the basis of a two phase composite, using the DSC measurements as a quantitative measure of the proportions of the two phases. For example, taking the longitudinal moduli of the fibre phase and the recrystallised phase as 42 and 1 GPa, respectively, and the DSC data for hot compaction at 140 °C which showed 25% matrix phase, the predicted longitudinal modulus for the

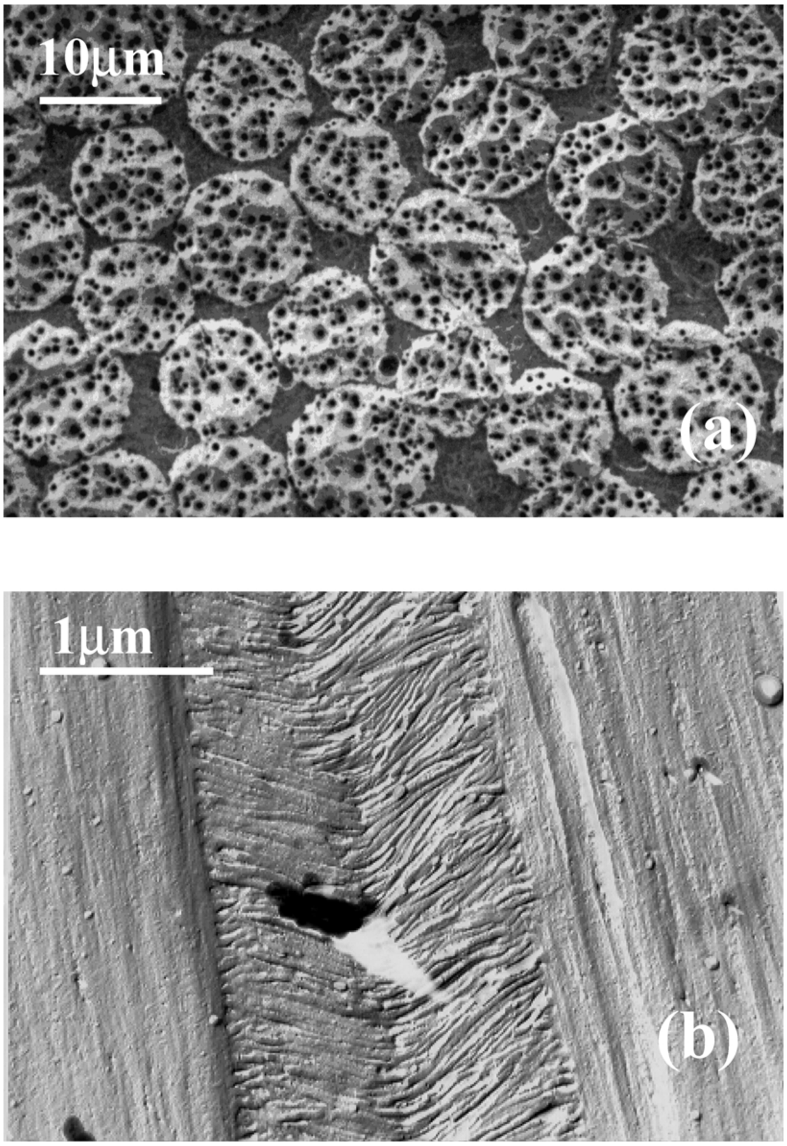

Fig. 4. Etched micrographs from unidirectional CERTRAN PE fibres. (a) SEM picture of a transverse section of compacted fibres. (b) TEM picture of an interstitial lamellar region and its junction with adjacent fibres.

compacted material is 31.8 GPa, compared with the measured value of 33 GPa.

3. Hot compaction—studies on other materials

Following the initial studies of the hot compaction of melt spun polyethylene fibres, further research has shown that conditions can be found for the successful compaction of a very wide range of oriented fibres and tapes, including gel spun polyethylene fibres (both Dyneema [15] and Spectra [16]), polyethylene terephthalate fibres [17,18], liquid crystalline polymer fibres [19] and fibrillated polypropylene tapes [20]. In a recent study, a new highly oriented melt spun polyethylene tape (Tensylon manufactured by Synthetic Industries) was found to have exceptional properties when compacted into a sheet. Table 2 shows a comparison of the properties of the four woven polyethylene materials studied throughout this research programme (Certran, Dyneema, Spectra and Tensylon). As the modulus of the original oriented material increased it was found that the optimum compaction temperature also had to be increased. At the optimum temperature, the percentage of melted matrix material was found to be around 30%. Interestingly, the Dyneema fibres studied were found to have a skin with a higher melting point compared to the interior. Similar regions of epitaxial recrystallisation were found in the compacted Dyneema samples to those found in the melt spun CERTRAN samples (e.g. Fig. 4b), although unfortunately they were found in the interior of the fibres rather than at the fibre's surface. For this reason the compaction of these fibres produced a poorly bonded structure and inferior properties. This study showed that in the case of the Dyneema fibres, the morphology of the

Table 2
Properties of the optimum compacted woven PE samples

Reinforcement name	Certran	Dyneema	Spectra	Tensylon
Optimum compaction temperature (°C)	138.5	150.5	151	153
Original fibre/tape modulus (GPa)	42	70	70	88
Compacted sheet tensile modulus (GPa)	10.0	7	21	30
Compacted sheet ultimate tensile strength (MPa)	160	250	460	400
Peel strength (N/10 mm)	8	5.2	7.4	9

original oriented material could influence the hot compaction behaviour. As described above, the properties of these compacted sheets could also be understood quantitatively in terms of a simple rule of mixtures. For instance for the woven compacted Tensylon sample the theoretical prediction was 29 GPa, in good agreement with the measured value of 30 GPa.

While the hot compaction of these highly oriented polyethylene fibres and tapes has continued to be of scientific interest, it was appreciated about five years ago that the best chance of commercial exploitation of this technology lay with polypropylene. For that reason the focus, both for fundamental and technological research had to change to look at the hot compaction behaviour of polypropylene. The first work in this area was again carried out in collaboration with our colleagues at Reading. The hot compaction behaviour of a commercially produced woven polypropylene cloth was studied in detail using a combination of mechanical tests, DSC measurements and morphology [20,21]. These studies showed that the morphology of hot compacted polypropylene was very similar to that seen in polyethylene, with a matrix phase epitaxially recrystallised onto the oriented tapes (Fig. 5a). As with PE, the recrystallised lamellae growing from the original oriented material are highly aligned and grow out to meet with another similar region from an adjacent tape (the boundary between a tape and the epitaxial recrystallised matrix material is shown by the white arrow). Fig. 5b shows a lower magnification picture of a bundle of tapes that have been compacted. This sample was made at a temperature higher than optimum, making the epitaxially recrystallised material more apparent. It can be seen how the recrystallised matrix material has filled in all the gaps in the structure, forming a homogeneous well-bonded structure. In the region just above centre, end on row structures have been formed in a region where the gap between the tapes was too large to be crossed by the epitaxial material.

Two key issues have arisen from the polypropylene studies which are different to the early PE studies. Firstly, PP in general does not have such a refined crystalline structure as PE, with the result that it is more sensitive to elevated temperatures close to the melt (i.e. the compaction temperature) and also shows a greater superheating effect. As a result of its high crystallinity, PE is stable to temperatures only a few degrees below the melting range, and the peak melting point does not change significantly with temperature. Conversely, polypropylene can show significant shrinkage at temperatures 100 °C below the melting range, and the peak melting temperature is very sensitive to constraint and applied pressure. DSC studies also showed that the compaction process can have an annealing aspect, with significant changes in the overall crystalline structure seen in PP, particularly an increase in the total crystallinity [20].

The second key aspect is the role of the matrix phase. In PE the oriented phase is characterized by a very high modulus (40–90 GPa) and a relatively low strain to failure (~2–4%): in comparison the matrix shows a very low modulus (1 GPa) and is ductile. Consequently the properties of the compacted sheet are dominated by the oriented phase and the matrix properties can almost be neglected. In PP the situation is different. In this case the oriented phase has a modulus between 10 and 15 GPa and the matrix around 1.5 GPa, so the matrix can make a significant contribution to the properties of the sheet. Additionally the oriented PP fibres or tapes have a high failure strain (~15%) and so it is imperative that the matrix remain coherent until the oriented phase fails.

These issues have been investigated in detail in two recent publications [22,23] which have once again combined mechanical measurements with DSC and morphological studies to investigate the hot compaction behaviour of a range of commercially available woven oriented PP cloths. The five materials studied used different shaped oriented components (fibres and tapes), different molecular weight polymers and various weave styles, allowing the importance of these factors on hot compaction behaviour to be studied. The key finding of this study, was the realisation of the importance of ductility of the matrix phase for subsequent behaviour of the compacted PP sheets, in particular the large strain behaviour which is vital for good impact performance. Although low molecular weight polymers are often used for spinning and drawing to high draw ratios, when such a material is selectively melted during the hot compaction procedure, it can form a poor matrix for the subsequent composite due to its brittle nature. Morphological studies showed that the lower molecular weight grades also exuded much more material compared to a high molecular weight polymer and that this lower MW material could recrystallise to form a weak transcrystalline boundary layer. The best hot compacted sheet performance was found for woven oriented tapes made from a polymer of

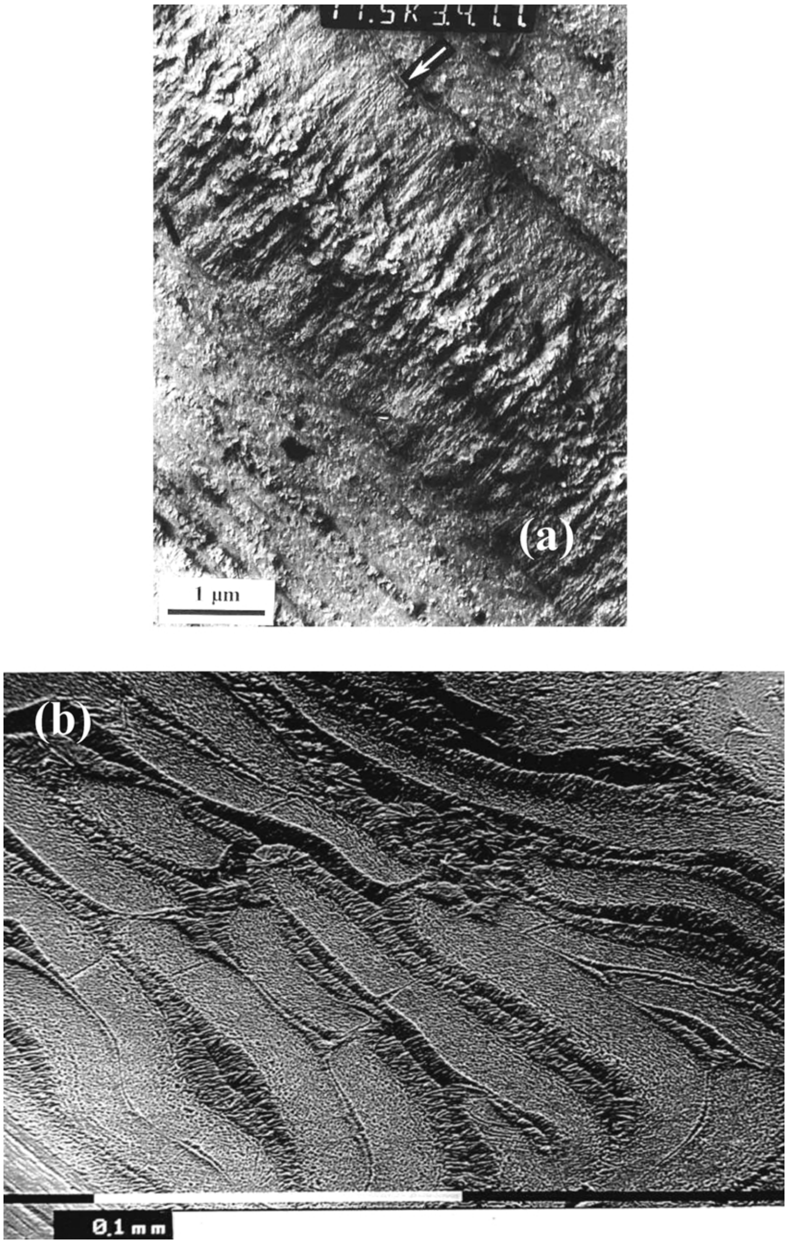

Fig. 5. Etched SEM micrographs of compacted polypropylene fibrillated tapes. (a) Details of epitaxial crystallisation, (b) section across a bundle of tapes.

$M_w > 300{,}000$. Such polymers were found to produce a ductile matrix on melting and recrystallisation.

Fig. 6 shows typical stress–strain curves for three materials, namely an original oriented tape, the behaviour of this tape when completely melted (i.e. the matrix phase) and the stress–strain behaviour of a hot compacted sheet composed of layers woven from the oriented tape. It is clear that the behaviour of the hot compacted sheet lies between that of the oriented tape and the isotropic matrix. We can develop a simple rule of mixtures to predict the properties of hot compacted woven sheets as described above for unidirectionally aligned compacted sheets.

Assuming continuity of strain between the phases, for a unidirectional arrangement of the oriented phase we can write the in-plane modulus of the composite, $E_{\mathrm{composite}}$, in terms of the modulus of the oriented (E_{O}) and matrix (E_{M}) phases, as follows

$$E_{\mathrm{composite}} = E_{\mathrm{O}} V_{\mathrm{O}} + E_{\mathrm{M}} V_{\mathrm{M}}$$

For a woven structure of tapes, the oriented component is now split into two halves, one half for the longitudinal tapes (E_{L}) and one for the transverse tapes (E_{T}), as follows

$$E_{\mathrm{composite}} = E_{\mathrm{L}} \frac{V_{\mathrm{O}}}{2} + E_{\mathrm{T}} \frac{V_{\mathrm{O}}}{2} + E_{\mathrm{M}} V_{\mathrm{M}}$$

In general orientation does not change the transverse modulus E_{T} significantly from the isotropic polymer so

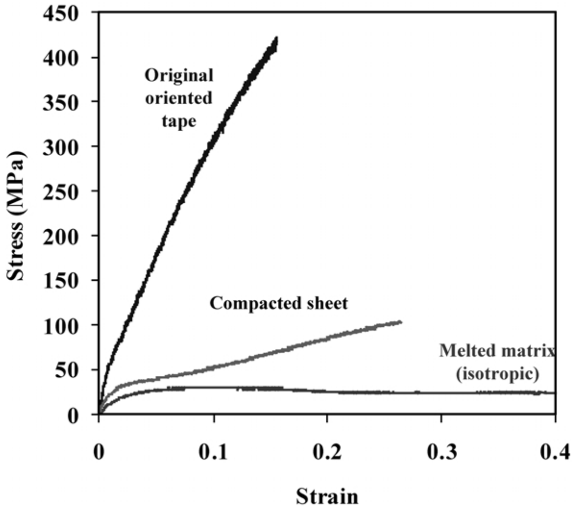

Fig. 6. A comparison of the stress–strain behaviour of the original oriented tapes, the melted matrix material and the hot compacted composite.

we can make the assumption that the transverse modulus of an oriented tape is the same as the polymer E_M. This leads to the following prediction (which is an upper bound as it assumes the woven tapes are perfectly straight, i.e. no crimp) for the in-plane modulus of a woven compacted sheet.

$$E_{\text{composite}} = E_L \frac{V_O}{2} + \frac{E_M}{2}(1 + V_M)$$

Table 3 shows that this simple model gives an excellent prediction of the in-plane modulus for both compacted woven PP tapes and for compacted woven PE tapes (the Tensylon material described earlier).

The most recent polymer to be studied in detail is polyethylene terephthalate [18]. The major challenge with PET is hydrolytic degradation, which at the temperature required for successful hot compaction (~250 °C) can occur very rapidly: at 255 °C the molecular weight can drop by 50% in 20 min compared to 18 h for the same percentage fall at 140 °C. A significant fall in molecular weight leads to embrittlement of the recrystallised matrix phase with the same effect as described above for the low molecular weight PP grades, so this is obviously undesirable. It was found that good samples, with a ductile matrix phase, could be made by either keeping the dwell time at the compaction temperature to a minimum (~2 min) or drying the woven cloth first whereby a longer dwell time (~5 min) could then be used. Fracture surfaces from compacted PET samples (e.g. Fig. 7) showed evidence that the matrix phase epitaxially recrystallised onto the oriented fibres as seen in PE and PP.

Table 3
Predictions of in-plane compacted sheet modulus (based on the phase properties) in comparison with experimental measurements

	Polypropylene	Polyethylene
Original tape modulus (GPa)	11	88
Melted matrix modulus (GPa)	1.2	0.51
Predicted compacted sheet modulus (GPa)	4.9 ± 0.30	29.4 ± 2.2
Measured compacted sheet modulus (GPa)	5.00 ± 0.1	30 ± 2

Using a volume fraction of 30 ± 5%.

An important issue with compacted sheets is to establish how the mechanical properties compare to other materials. In this respect we have often compared the properties of compacted sheets with those of an isotropic polymer and a glass fibre filled polymer. Such a comparison for PET showed that while the majority of the properties lay between these two materials (i.e. isotropic PET and glass fibre filled PET), the impact strength was much higher than either material. As we will see shortly confirmed for PP, it is this property of hot compacted sheets, which is most outstanding. Table 4 compares the mechanical properties of optimum samples of compacted PE, PP and PET.

4. Elastic anisotropy of hot compacted sheets

Returning for the moment to the early unidirectional fibre studies, we quickly appreciated that if only a small fraction of the oriented phase was melted, then a compacted sheet is a way of obtaining a large block of material with similar mechanical properties to the original oriented fibres. This then provides a way of measuring the elastic properties of the oriented fibres, something that is normally quite difficult to achieve, particularly for the transverse constants. The measurements of the elastic constants were carried out using the ultrasonic immersion technique (2.25 MHz), developed at Leeds by Lord [24] based on the original work of Read and Dean [25]. For these measurements transverse strength is of minor importance, so compaction temperatures were chosen to be the lowest for perfect compaction, permitting maximum retention of fibre properties.

Initial experiments using the melt spun Certran fibres [26], and using different compaction temperatures to give a

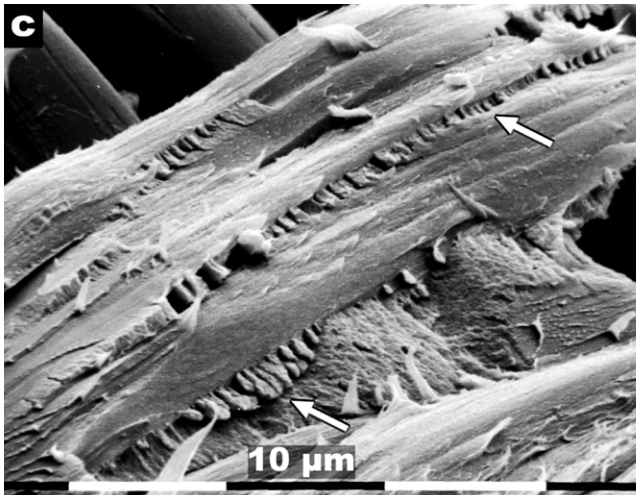

Fig. 7. Peel fracture surface from compacted woven PET sheet showing epitaxial recrystallised matrix (white arrow).

Table 4
A comparison of typical properties of compacted PET, PE and PP sheets

	ASTM standard test	PET	Polypropylene	PE
Density (kg/m^3)		1400	910	970
Tensile modulus (GPa)	D638M	5.82	5.06	28
Tensile strength (MPa)	D638M	130	182	370
Heat deflection temperature (1820 kPa) (°C)	D648	108	102	132
Thermal expansion ($\times 10^{-6}$/°C)	D696	26.4	41	-1.5
Notched Izod strength (20 °C) (J/m)	D256	2020	4760	1340

range of fractions of the oriented fibre phase, showed that only the stiffness constant in the fibre direction, here designated C_{33}, (or the longitudinal Young's modulus E_{33}) is very sensitive to the fibre volume fraction so comparisons between different fibres can be made to a good first approximation using only the 'optimum' compacted sheets. Results for the five fibre types measured (PE, PP, PET and LCP) are collated in Table 5 and show remarkable similarity in terms of the patterns of anisotropy for the different oriented fibres. As is well known, the high values of E_{33} for polyethylene and the liquid crystalline polymer (LCP) relate to the very high degree of molecular alignment combined with the comparatively straight molecular chains so that the modulus relates to intramolecular bond stretching and bond bending rather than intermolecular dispersion forces which determine the other elastic constants. It is particularly interesting that whereas in all cases ν_{13} is less than 0.5, ν_{12} is invariably greater than 0.5. This pattern of anisotropy is consistent with an 'ideal' fibre-reinforced material where a matrix with very low shear modulus is reinforced by very stiff fibres. This result shows that the fibres themselves are akin to a fibre reinforced composite. The Poisson's ratio ν_{13} of ~ 0.5 implies that there is only a very small volume contraction for stress applied along the fibre axis. On the other hand $\nu_{12} \approx 0.7$ implies that applications of stress transverse to the fibre axis causes almost no deformation in the very stiff 3 direction i.e. the deformation is accommodated by pure shear in the 12 plane.

It is of interest to compare these results on hot compacted sheets with other materials, especially die-drawn rods and fibre reinforced composites. In all cases the comparisons show remarkable similarity. The results are shown in Table 6 and confirm that the hot compaction process has been applied satisfactorily. Compared with die-drawing the hot compaction process has the advantage of being extended to woven fabrics to produce balanced structures very readily. Compared with conventional fibre/epoxy composites there are major advantages in terms of recycling and postformability to be discussed later. The principal conclusion to note at this stage is that hot compaction can produce structures in larger section which reflect the advantages of highly oriented fibres in terms of stiffness (and as will be seen, strength).

Table 5
The elastic properties of compacted plates, and hence the original oriented fibres

	E_{33}	E_{11}	ν_{13}	ν_{12}	G_{13}
Certran (PE)	57.7	4.68	0.45	0.55	1.63
Dyneema (PE)	74.3	4.31	0.47	0.57	1.36
PET	14.9	3.70	0.39	0.58	1.52
PP	11.0	2.41	0.39	0.58	1.52
LCP	97.2	3.24	0.48	0.73	1.3

5. Thermal expansion behaviour

Thermal expansion, or dimensional stability, has proved to be of both scientific interest and practical importance for industrial applications. For most applications a low thermal expansion is desirable and in some instances, such as internal automotive structures, it should be similar to that of a metal. In oriented polymers, the situation is complicated by the possibilities of frozen-in network stresses and creep under load, both of which can be either reversible or permanent. A further complication is the anisotropic nature of the thermal expansion behaviour in an oriented polymer. For example, in polyethylene fibres there is a low negative co-efficient of thermal expansion in the chain axis direction (the fibre axis) typically $\sim -10^{-5}\ \mathrm{K}^{-1}$ and a much larger positive coefficient, typically $+10^{4}\ \mathrm{K}^{-1}$ transverse to the fibre axis.

For practical applications where balanced in plane properties are required, the most useful form of starting material for hot compaction is a woven textile cloth, using either highly oriented fibres or tapes, where the greater surface area can give some advantages in terms of the interlayer strength (the peel strength) of the hot compacted sheet. Detailed studies of thermal expansion behaviour have been undertaken [27] for hot compacted polypropylene

Table 6
The elastic properties of compacted Certran PE plates in comparison with a die drawn PE sheet and a polyethylene fibre reinforced epoxy composite (fibre volume fraction 55%)

	C_{33}	C_{11}	C_{13}	C_{12}	C_{44}
Hot compacted Certran (PE)	62.3	7.16	5.09	4.15	1.63
Die drawn PE sheet	66.0	6.90	4.40	3.90	1.60
PE/epoxy composite	54.8	7.62	5.89	4.39	1.71

sheet which has an excellent cost/performance balance for large volume applications such as automotives and hot compacted polyethylene sheets where there are important niche applications such as radome covers. In both cases results were obtained for sheets prepared from unidirectional arrays of fibres or tapes and from woven textile fabrics. The proposal here was that the hot compacted woven sheets could be modelled in terms of a modified 0/90 laminate, where the properties of each individual lamina are the same as a unidirectional sample.

The thermal expansion measurements were carried out using custom built equipment developed at Leeds University and the results were considered in the light of a simple theoretical treatment. Following Chou and co-workers e.g. [28] the woven structure of the compacted sheet was approximated to a representative volume element (RVE) of a cube of unit dimensions made up of blocks whose properties are those of a unidirectional composite. Fig. 8 shows how the RVE consists of four blocks. Blocks A and B are basically a cross-ply laminate; as the original woven fabric is of plain weave construction there are equal amounts of A and B. Blocks C and D lie round the sides of A and B and represent the regions where the weft has to pass under the warp. The width of the blocks C and D, denoted as x, is the only unknown quantity in the model. Although pictures of a transverse section of the compacted sheet taken using the permanganic etching technique show a far from regular structure, results that follow suggest that the most likely value of x is the thickness of the unidirectional layer, so that the fibre axis can be placed at 45° to the 2 axis for these blocks.

Two different simulations were carried out. In Case 1 the RVE was subjected to a unit increase in temperature, which allowed the in-plane and out-of-plane thermal expansion coefficients to be calculated. In Case 2, a unit stress was applied to the RVE in the 1 direction so that the in-plane modulus could be calculated. (Note that because the RVE is not symmetrical there will be a difference between predictions for the 1 and 3 direction; in practice this difference is very small). The calculations involve satisfying equilibrium stress conditions and compatibility equations between the different blocks in the RVE. These equations are linear and were solved by matrix multiplication using an Excel spreadsheet.

The strategy for the simulations was as follows: vary the value of x for CASE 2 to give the same value of the in-plane modulus as measured experimentally and then use the same value of x to predict the thermal expansion using CASE 1 loading. The measured values for the thermal and mechanical properties of the compacted sheets, together with model predictions are shown in Tables 7 and 8. For polypropylene, the measured in-plane thermal expansion of the compacted sheet is $73 \times 10^{-6}\ \mathrm{K}^{-1}$ which is lower than that for isotropic polypropylene ($100 \times 10^{-6}\ \mathrm{K}^{-1}$) but much larger than most metals. The out-of-plane expansion for the sheet is larger at $118 \times 10^{-6}\ \mathrm{K}^{-1}$. The simplest prediction for the in-plane properties would be to assume a series model with no side blocks ($x = 0$), which would be an isostress prediction. This gives too high values for both modulus and thermal expansion as it does not take into account either the woven structure or the elastic constraints between the layers. If a parallel model is used to include the elastic constraints but with x kept at zero (equivalent to a 0/90 laminate structure), this gives a good prediction for the thermal expansion but overpredicts the modulus, as would be expected. If we include both the elastic constraint and the woven structure, then a value of $x = 0.062$ predicts the correct modulus and gives a good prediction of the thermal expansion values. If we assume that the thickness of the cross over zone x is determined by the thickness of the individual layers t, then if the width of tapes is W, we have

$$x = \frac{t}{t + W}$$

The measured values of t and W for the polypropylene fabric gave a value for x of 0.077 which is in very satisfactory agreement with the model prediction of x.

In the case of the hot compacted polyethylene sheets the thermal and mechanical properties show much greater anisotropy. The unidirectional sheet shows a negative thermal expansion of $-15 \times 10^{-6}\ \mathrm{K}^{-1}$ in the fibre direction and $+120 \times 10^{-6}\ \mathrm{K}^{-1}$ in the transverse directions. For the woven sample an in-plane value of $16 \times 10^{-6}\ \mathrm{K}^{-1}$ is measured which is similar to that for metals. The various model predictions are similar to these for polypropylene but here the elastic constraint plays a much greater role than in polypropylene as would be expected because of the large mechanical anisotropy. The best estimate requires the

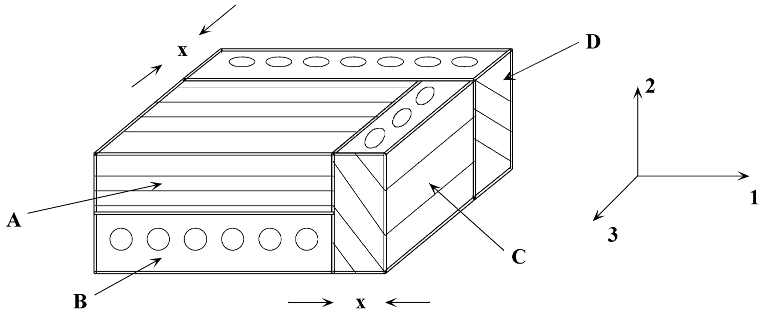

Fig. 8. Representative volume element for modelling the thermal expansion behaviour of a woven hot compacted sheet.

Table 7
A comparison of the measured values and the model predictions for compacted polypropylene sheet

	Measured	Series	Parallel	Model
In plane modulus (GPa)	3.5	4.01	4.05	3.5
In plane thermal expansion (× 10^{-6} K^{-1})	73	84	74.4	76.8 (1 axis), 76.3 (3 axis)
Out-of-plane thermal expansion (× 10^{-6} K^{-1})	118		135	128
$x = t/(t + W)$	0.077	0	0	0.062

inclusion of the cross layer zone: the value of x needed to predict the in-plane modulus of 9.81 GPa is 0.23 which agrees well with a value of 0.21 determined from the tow width and the cloth thickness. Using the value of $x = 0.23$ gives good predictions of the thermal expansions of the compacted PE sheet, much better than either an isostress or isostrain prediction. This work shows that the woven nature of the material must be taken into account when modelling the thermoelastic properties, but that a simple model can give good predictions and aid understanding of the behaviour.

6. Commercial exploitation

The early studies above have described the establishment of a science base for the hot compaction process through a combination of mechanical testing and morphological studies, in the main looking at polyethylene but also for other oriented polymers. As the research has expanded into more application based areas it has become clear that the most likely candidate polymer for commercial exploitation was polypropylene, and so research over the last few years has concentrated on the hot compaction behaviour of this material. The key questions to be answered before commercialisation could proceed were, firstly, what is the portfolio of mechanical properties that this material can offer and secondly could the hot compacted sheet be thermoformed into a variety of shapes. In order to obtain material of sufficient size to answer these questions, two routes were pursued. In the first, large size material, ~2 m × 1 m was produced in a variety of thicknesses in a local autoclave. In the second, belt press trials were carried out which also helped to determine the design for a continuous process. This facility is now in operation in Gronau, Germany following the licensing of the hot compaction technology to BP AMOCO and commercial grade material (Curv™) has recently become available. The feedstock for the commercial material is a specially designed fabric made from woven oriented polypropylene tapes. Table 9 shows a comparison of the properties of commercial compacted woven polypropylene (Curv™) in comparison with isotropic PP, random short glass fibre filled PP and continuous glass fibre filled PP. From these results it is seen that compacted PP sheet shows an exciting combination of properties, with the density of an unfilled polymer, a strength and modulus lying between short glass fibre and continuous fibre reinforced PP and an impact strength greater than all the other PP based materials. The impact strength is perhaps the most outstanding property of hot compacted sheet materials, and is a consequence of the combination of a high failure strength and a high failure strain. Importantly, the high impact strength is retained, and is in fact improved upon, at temperatures as low as −40 °C, in contrast to other PP based materials which tend to show brittle behaviour at low temperatures. The preferred molecular orientation of the original PP tapes, which is substantially maintained through the compaction process, reduces the embrittling effect of going below the glass transition for PP which is around 0 °C.

A very important feature of the hot compacted sheets, vital for commercial exploitation, is their thermoformability, which means that under appropriate conditions the sheets can be post formed into appropriate shapes to make commercial products. Examples of such products, whose properties will be discussed in detail in a further section of this review article are loudspeaker cones and automotive parts, notably undertrays.

Studies have therefore been undertaken [29] directed at identifying the key factors determining satisfactory postforming, partly by determining the stress–strain characteristics of the compacted sheets at temperatures where postforming can be achieved and partly by undertaking a simple thermoforming operation where sheet can be postformed into a hemisphere under controlled laboratory conditions.

Table 8
A comparison of the measured values and the model predictions for compacted polyethylene sheet (melt spun Certran fibres)

	Measured	Series	Parallel	Model
In plane modulus (GPa)	9.81	23.5	23.8	9.81
In plane thermal expansion (× 10-6K-1)	16	52.5	−2.8	19.0 (1 axis) 14.5 (3 axis)
Out-of-plane thermal expansion (× 10-6K-1)	157	120	164	137
$x = t/(t + W)$	0.21	0	0	0.23

Table 9
A comparison of the mechanical properties of PP based materials

		Curv™ hot compacted PP sheet	Isotropic PP momopolymer	Random mat short glass/PP 40 wt% fibre	Continuous sheet glass/PP 60 wt% fibre
Density (kg/m^3)		920	900	1185	1490
Notched Izod impact strength (J/m)		4750 (20 °C), 7500 (−40 °C)	200	672	1600
Tensile strength (MPa)		180	27	99	340
Tensile modulus (GPa)		5.0	1.12	3.5–5.8	13
Heat deflection temperature	°C/455 kPa	160	110	154	155
	°C/1820 kPa	102	68		
Thermal expansion (10^{-6}/°C)		41	96	27	21

Comparison data for other materials taken from http://www.matweb.com. Quoted values are averages of all commercially available grades. Compacted PP made on a pilot plant—http://www.curvonline.com

Fig. 9a shows a schematic diagram of the stress–strain curve of a compacted polypropylene sheet. There is an initial elastic region where the modulus is high. At ~5% strain a yield point is seen above which the stress continues to rise at a lower rate until failure occurs. This region defines 'a post-yield modulus'. It includes significant plastic deformation and shows that considerable forces are required to thermoform these compacted sheets. Experiments (Fig. 9b) show that the initial elastic modulus decreases rapidly with increasing temperature, whereas the post-yield modulus shows a less, but significant, decrease which is very important in determining the forces required for postforming. Another key processing variable is the failure strain which increases from ~60% at 140 °C to over 80% at 170 °C.

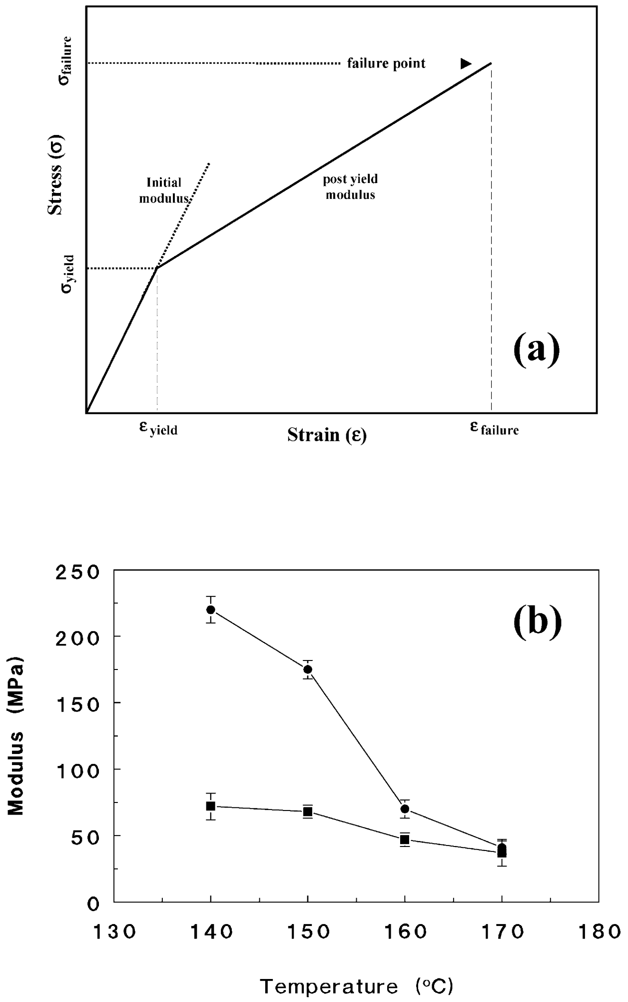

Fig. 9. Thermoforming details (a) a schematic diagram of a stress–strain curve for hot compacted PP sheet, (b) dependence of initial modulus (●) and post-yield modulus (■) on test temperature.

The thermoforming tests were carried out using a specially designed rig, based on that reported by Hou [30] consisting of male and female hemispherical moulds which fits inside an Instron oven, allowing the 'forming temperature' to be accurately controlled. Using this rig, postforming tests were undertaken on the hot compacted sheets with temperature and closing speed (essentially the cross-head speed of the hemispherical male mould controlled by the Instron testing machine) as the key variables. As anticipated from the tensile tests on the hot compacted sheets, temperature was the most important variable with the forming force falling by 300% when going from 140 to 170 °C.

The results of the forming trials showed that it is most important to recognise the limitations of the strength of the melted and recrystallised material which binds the oriented tapes together and to ensure that the tapes are not melted during the forming process. The tensile tests on the sheets show that the higher the temperature the greater the maximum possible strain and the lower the resistance to deformation. There is, however, the awkward issue as to whether there should be any remelting of the recrystallised polymer which forms the matrix of the hot compacted structure.

These observations have led us to propose two alternative strategies for postforming. First, to treat the hot compacted sheet as a homogeneous anisotropic structure and postform at ~150 °C, which is below the melting point of the recrystallised matrix material. Secondly, and this permits greater deformations to be imposed, to treat the sheet as a fibre reinforced material with a lower melting matrix and postform above the melting point of this phase but below the melting point of the oriented tapes: ~170 °C

Table 10
A comparison of hot compacted PP and GMT undershields

	Hot compacted PP Curv™	GMT
Weight (g)	900	1200
Puncture impact energy at 20 °C (J)	31.6	16.8
Notched Izod at 20 °C (J/m)	4750	750
Notched Izod at −40 °C	7500 J/m	Brittle
Abrasion resistance (time to create 10 mm hole on standard 2 mm test sample)	>3 h	1 h 40 min

appears a good choice. On cooling, the recrystallised phase which has been melted recrystallises again to bind the structure into its postformed shape.

7. Practical applications

There are many incentives to the application of hot compaction, including recyclability, postformability and a very satisfactory portfolio of mechanical properties. For each major application identified so far, there is always one key advantage over existing materials, in addition to these very desirable general features. Four examples of current and/or potential applications of the hot compaction technology will be described to highlight these various performance advantages. Pictures of these four examples are shown in Fig. 10 and are as follows: (a) an automotive undertray made from hot compacted PP sheet (Curv™): (b) a NIKE soccer shinguard made from hot compacted PP sheet (Curv™): (c) a helicopter radome cover made from hot compacted crosslinked Certran PE fibres: (d) a loudspeaker cone made from hot compacted PP sheet.

7.1. Automotive undertray

For this application the key properties are the combination of a low density, excellent impact performance (even at −40 °C), good abrasion resistance, thermoformability and the potential for recycling. Recently, abrasion tests have been carried out by Daimler Chrysler [31], comparing

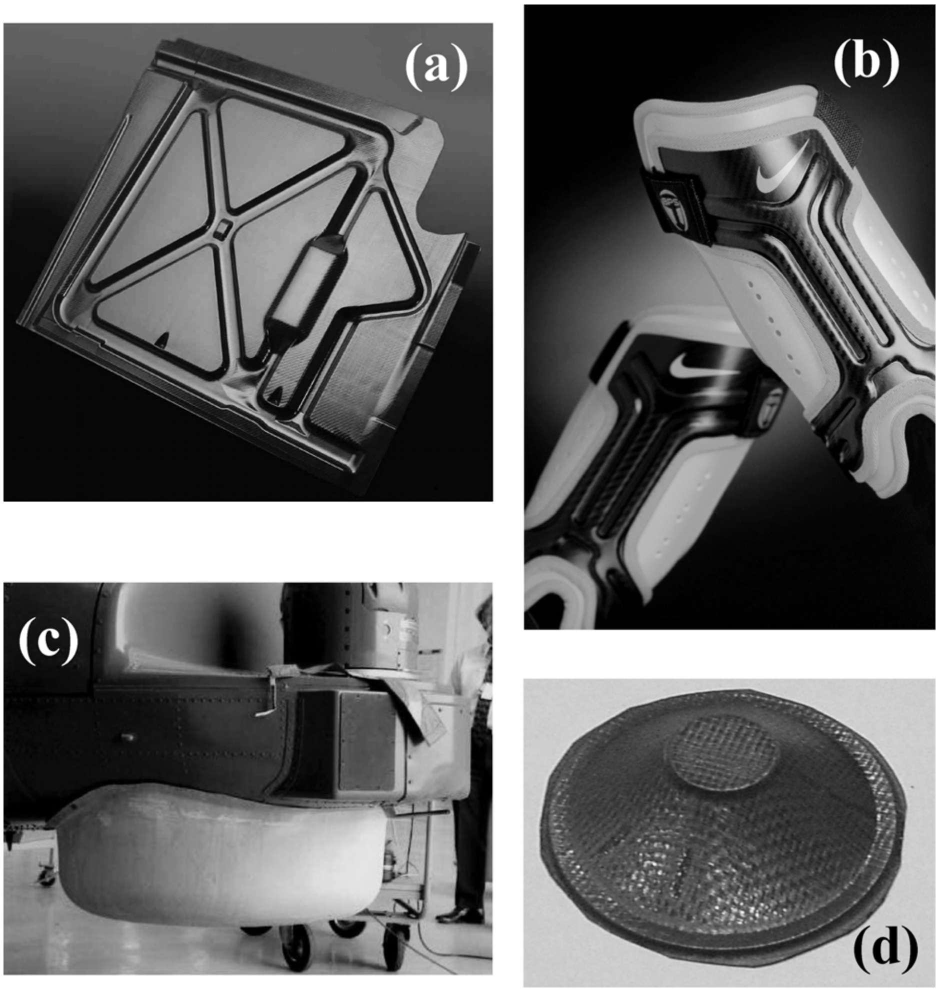

Fig. 10. Examples of applications for hot compacted sheets: (a) automotive undertray, (b) NIKE soccer shinguard, (c) helicopter radome cover, (d) loudspeaker cone (Picture (a) by kind permission of BP AMOCO, Picture (b) by kind permission of BP AMOCO, Picture (c) by kind permission of GKN Westland Helicopters.).

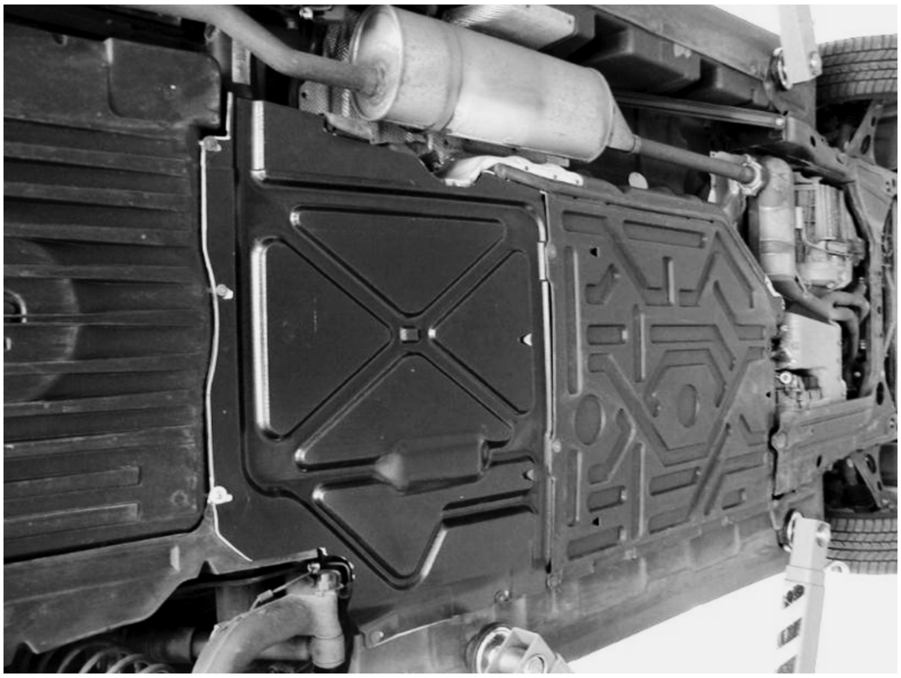

Fig. 11. On vehicle installation of hot compacted PP undertray (Picture by kind permission of BP AMOCO.).

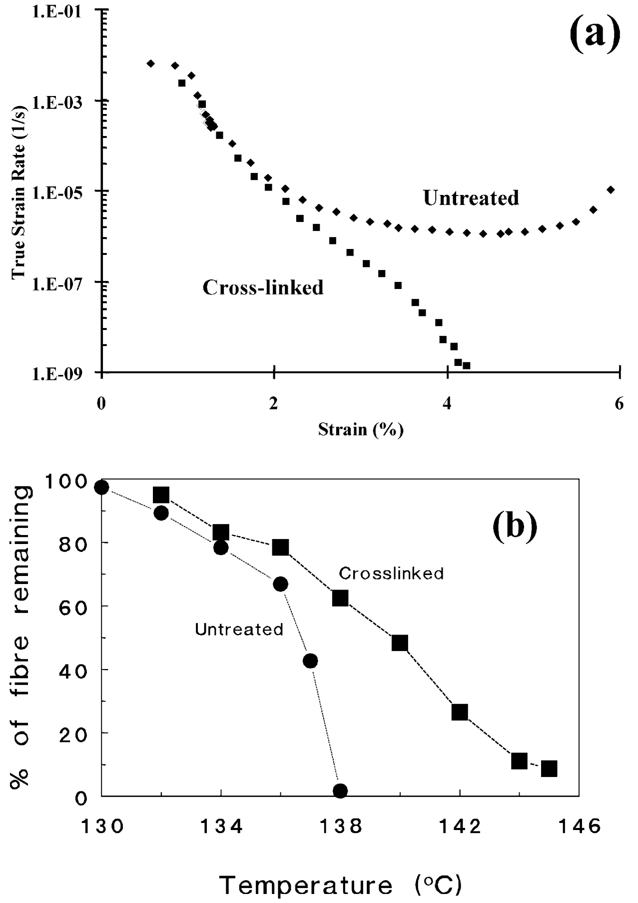

Fig. 12. The effect of cross linking on melt spun Certran PE fibres (a) Sherby–Dorn plots showing reduced creep for cross linked fibres, (b) percentage melting versus compaction temperature.

Curv™ hot compacted PP sheet with three other materials, a conventional chopped glass mat/PP composite (GMT) with 20% glass fibre content (GMT 20), a 'heavy duty' GMT with 35% glass fibre and additional PET reinforcing fabric to improve its abrasion resistance (GMT 35) and a natural fibre reinforced PP (NMT). The results indicate that Curv™ compacted PP has the highest resistance against abrasion by stones of these materials tested. The thermoformed undertray part has since been installed onto a vehicle and has passed the on-vehicle trials successfully. In addition to the ongoing vehicle trials (Fig. 11 shows an on-vehicle installation of a hot compacted PP undertray), mechanical tests have been carried out to compare the mechanical properties of the Curv™ and GMT undertrays. The results of these tests, shown in Table 10, confirm that the compacted PP undertray out performs the GMT part, as well as being lighter.

7.2. Nike shinguard

For this application it is the combination of low density and excellent impact performance which makes hot compacted PP a candidate for sports armour/protection. The first application to make use of this material is for a range of Nike shinguards. The finished components, which are now on sale combine CURV™ with a foam to produce a component which outperforms other candidate combinations.

7.3. Helicopter radome cover

Initial attempts at commercialisation focussed on the possible use of hot compacted polyethylene for radome covers. The very low absorption of electromagnetic radiation for the 100% polyethylene material compares very favourably with that of previous materials, most usually polyethylene fibres with an epoxy resin matrix. Recognising that creep at high temperatures might be a limitation, the polyethylene fabrics were cross-linked by γ-irradiation in an atmosphere of acetylene [32], a process established in previous research at Leeds [33]. As shown by the Sherby–Dorn plot in Fig. 12a, cross-linking produces a major reduction in the creep of the hot compacted sheets and there is essentially no reduction in other mechanical properties [33]. The cross-linking does also produce an additional advantage for the processing of the fabric by hot compaction. As shown in Fig. 12b, whereas the unirradiated PE fibre loses its fibre structure above 137 °C, the cross-linked fibre retains its structure to much higher temperatures. This result is beneficial because it permits a wider processing window for hot compaction. An example of a radome cover, produced in collaboration with GKN Westland helicopters, is shown in Fig. 10c.

7.4. Loudspeaker cones

An unanticipated application for the hot compaction technology is for loudspeaker cones where it was found that the postformed polypropylene sheets had an ideal combination of stiffness and damping [34]. Fig. 13 shows a plot of sound velocity versus mechanical loss factor for a range of materials. It can be seen that hot compacted polypropylene lies in the correct area of the plot for good acoustic performance (top right is the optimum). This result gives some credence to the known practical result which was first demonstrated by the performance of Wilson Benesch loudspeakers.

In an attempt to gain more quantitative understanding recent research in collaboration with M. Jenkins and I Hay at Birmingham University has addressed the acoustic performance of hot compacted sheets of polypropylene and polyethylene. The results for polypropylene confirm that there is a very uniform attenuation over a wide frequency range and it is this coupled with the modest level of damping which gives excellent performance for cone loudspeakers. The polyethylene results, on the other hand, suggest that for flat loudspeakers where a very low level of damping is desirable, hot compacted polyethylene would be a better choice.

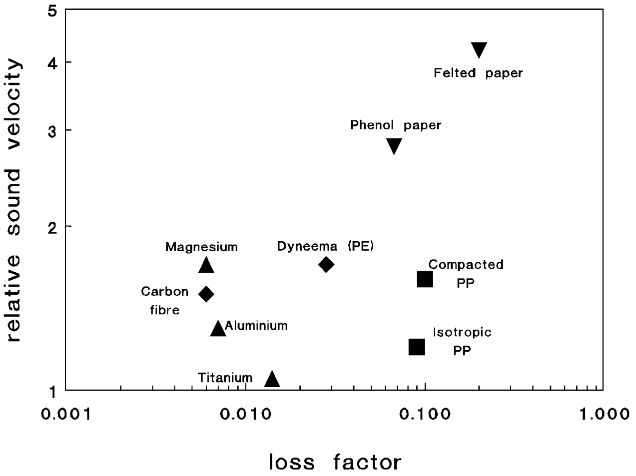

Fig. 13. Relative sound velocity versus loss factor for loudspeaker materials.

8. Conclusions

The hot compaction project at Leeds University has been an intimate mix of basic science and technological development. The initial stimulus came from the setting up of the IRC in Polymer Science and Technology in 1989, with the explicit aim of novel developments outside the gambit of existing research at Leeds. Discovery was given a free rein, and the success of this project shows the value of this strategy.

With regard to the science of hot compaction it will be clear that the collaboration between the Leeds team with its expertise on polymer processing and mechanical properties and the Reading team with its expertise in electron microscopy and polymer morphology has played a vital role. It is also the case that the science has been greatly stimulated by the industrial developments, which were given extra impetus by the activities of the incubation company, Vantage Polymers Limited. This spin-off company enabled the production of significant quantities of hot compacted materials to be achieved, which proved to be the crucial step in bridging the gap between the small scale laboratory based scientific studies and full scale commercialisation. The present research continues to develop in two directions, exploring a wide range of starting polymers and addressing the engineering issues such as postforming.

Hot compaction continues to present many challenges in respect of both the science and the commercialisation. It has proved to be an excellent blend of basic polymer science and new composites technology, and it is hoped that this review article conveys some of the excitement of such a rich tapestry.

Acknowledgements

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Professor I. M. Ward received a D.Phil from Oxford University in 1954 for ESR studies of inorganic complexes and irradiated materials. From 1954–66 he undertook research at ICI Fibres Division, becoming Head of Basic Physics and an ICI Research Associate. After four years as Senior Lecturer in the Physics of Materials at Bristol University, he was appointed to a Chair of Physics at Leeds University in 1970 where he founded the Polymer Group. In 1989 Professor Ward became first Director of the IRC in Polymer Science and Technology. He is presently Research Professor Emeritus and Director of the Centre for Industrial Polymers. He was elected to the Royal Society in 1983 and has been awarded several medals by the Institute of Materials (Griffith, Swinburne) and the Institute of Physics (C.V. Boys, Glazebrook).