THE HOT COMPACTION OF WOVEN POLYETHYLENE TEREPHTHALATE MULTIFILAMENTS

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ABSTRACT

In this paper we describe the development of a process, and the resulting mechanical properties, for hot compacted sheet made from woven multifilaments of polyethylene terephthalate (PET). Exploration of the different processing variables showed that a key aspect was the time spent at the compaction temperature, termed the dwell time. Molecular weight measurements, based on intrinsic viscosity, showed that hydrolytic degradation occurred rapidly at the temperatures required for successful compaction, leading to embrittlement of the resulting materials with increasing dwell time. A combination of techniques was used to examine the mechanical properties and morphology of the optimum compacted sheets, including mechanical testing, DSC and SEM studies. These tests reinforced the view from previous studies on hot compacted polypropylene, of hot compacted sheets as self reinforced composites, whose behaviour is a combination of the properties of the two components, namely the original oriented multifilaments and the melted and recrystallised matrix. Other key findings from the research included confirmation of the importance of obtaining high ductility in the melted and recrystallised phase, promoted by using a high molecular weight or suppressing crystallinity during processing, and the proportionately high impact performance of hot compacted sheets, in comparison with other materials.

INTRODUCTION

Research at Leeds University, over a period of 14 years, has seen the development of new process for the production of polymer/polymer composites, which is termed 'hot compaction'. The work developed out of the strong interest at Leeds in developing routes for improvement of the properties of isotropic polymers by solid state deformation processes, where the aim is to achieve transformation of the original randomly oriented semi-crystalline morphology into a preferentially aligned structure. The aim of the hot compaction process is to exploit the outstanding mechanical properties of highly drawn polymer fibres or tapes to create a new class of single phase thermoplastic composites, without the requirement of matrix phase of a different chemical composition to bind the structure together. In this patented process [1], oriented fibres or tapes are compacted together to form a self-reinforced, thermoformable, 100% polymer sheet which retains a high proportion of the physical properties of the original oriented material. The essence of the process is to take arrays of oriented fibres or tapes and choose suitable conditions of temperature and pressure such that a thin skin of each tape is melted. On cooling, this molten material freezes, or recrystallises, to bind the structure together. The resulting hot compacted sheet is therefore composed of a single material of one chemical composition and by virtue of molecular continuity between the phases, has excellent fibre/matrix adhesion. Also, by virtue of melting the skin of each oriented tape, there are none of

the wetting problems which can often be a problem for traditional thermoplastic composites. A schematic of the hot compaction process is shown below in Figure 1
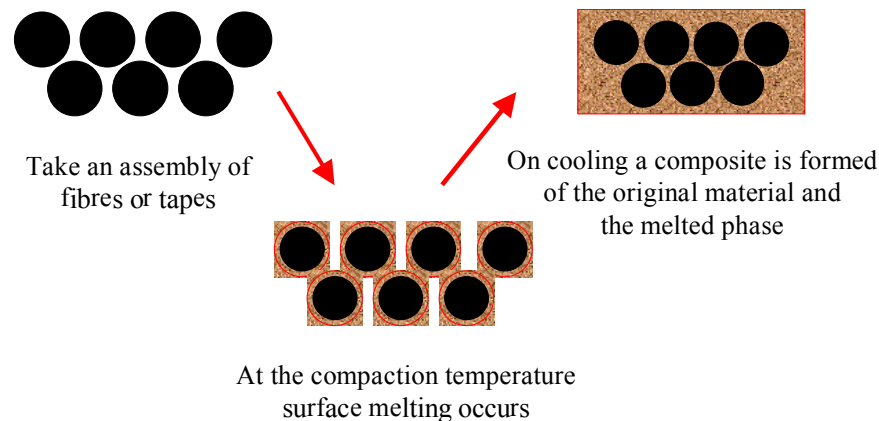

Figure 1:Schematic of the hot compaction process

The initial studies were carried out on highly oriented polyethylene fibres [2, 3]. Morphological studies using scanning electron microscopy (SEM) were able to show that selective melting of the fibres had occurred and that on cooling the melted material epitaxially crystallised onto the remaining portion of the oriented fibers.
More recently the work has concentrated on studying the hot compaction behaviour of polypropylene with a mixture of both fundamental studies [4, 5] and more application driven research [6, 7]. Ultimately, this work has led to the commercialisation of the hot compacted PP material by BP Amoco Fabrics Gmbh under the trade-name Curv[TM].

In this paper we describe recent experiments to investigate the hot compaction of polyethylene terephthalate (PET) multifilaments. PET is of interest because it is a widely available commercially produced oriented polymer, but also because it has the potential to show improved mechanical properties in some areas compared to hot compacted PP. Woven PET cloth was compacted over a range of conditions to establish the optimum compaction parameters. As with the polypropylene studies described above, a key issue to obtaining good compacted sheet properties was to develop procedures that ensured that the melted PET matrix phase was ductile after the procedure was completed. To ensure this, it was found that hydrolytic degradation had to be kept to a minimum, by performing the hot compaction procedure as rapidly as possible. The optimum compacted PET sheets were found to have mechanical properties that were comparable with the best hot compacted polypropylene sheets.

EXPERIMENTAL
The details of the woven PET cloth used in this programme are shown in Table 1 and Figure 1 below: the cloth was a plain weave construction (Figure 1 – the warp runs from the bottom left to the top right) composed of 1100 dtex filament bundles (0.21mm diameter), with a number average molecular weight for the base polymer of 25,150 g/mol. The number average molecular weight, of both the original fibres and the subsequently hot compacted sheets, was measured using the intrinsic viscosity technique via an Ubberlohde dilution viscometer suspended in a water bath at 25°C. 0.125 mg of each sample was dissolved in 25mg of the chosen solvent of

trifluoroacetic acid (TFA) and measurements were made of the time for a chosen volume of the mixture to flow through the viscometer in comparison with the pure solvent. Three further dilutions allowed the intrinsic viscosity to be determined by extrapolating to zero concentration. The number average molecular weight M_n, was then obtained from the Mark-Houwink relationship

$$\eta = kM_n^{\alpha} \qquad (1)$$

where η is the intrinsic viscosity, and k and a the Mark-Houwink parameters. For PET/TFA these values are given Moore and Sanderson [8] as 1.4×10^{-3} and 0.64 for k and a respectively, at 25°C.

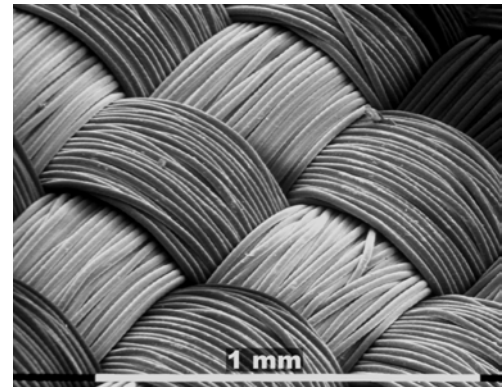|	
Number average molecular weight M_n (g/mol)	25150 ± 500
Filament linear density (dtex)	1100
Filament initial modulus (GPa)	14
Filament Breaking Strength (MPa)	1000
Filament Failure Strain (%)	19
Density (kg/m^3)	1400

Table 1: Details of the PET multifilaments

Figure 1: Woven PET cloth

Previous work in the department and by other workers [9-11] has established that hydrolytic degradation' can occur in PET (leading to a reduction in molecular weight and hence mechanical properties) and the rate of this depends on the temperature and the water content. A crucial aspect of the hot compaction of PET is therefore the ability to keep the assembly at the compaction temperature for the minimum possible time to inhibit hydrolytic degradation and secondly to cool the sample rapidly after compaction to promote ductility in the melted fraction. In order to achieve these goals, it proved necessary to develop a new variant of the standard batch technique described in the previous published work on the hot compaction of polypropylene where the compaction assembly was contained inside a matched metal mould. In order to reduce the overall cycle time in the present work, and to aid rapid cooling, the layers of PET cloth to be compacted were placed between brass plates, which therefore had a much lower thermal inertia compared to a thick metal mould assembly. The compaction procedure was therefore as follows. Firstly the layers of woven PET cloth (175mm square) were assembled between brass plates, with outer layers of PTFE release film and soft aluminium to aid release after compaction. The lay-up used was a 0/90 symmetric arrangement to even out the differences in the warp and weft tensions shown in Figure 1. A thermocouple was placed between the central two layers of cloth to allow the temperature of the assembly to be monitored during the compaction procedure. At this point either compaction proceeded immediately, or alternatively the assembly was placed into a vacuum oven set at 80°C overnight (16 hours) for drying before compaction.

For compaction, the hot press was first set to the appropriate compaction temperature and allowed to equilibrate. The assembly was then placed into the hot press, a pressure of 2.8MPa (400psi) was applied immediately to prevent any shrinkage, and the temperature of the assembly was monitored. Once the assembly reached the required temperature, it was left for a designated dwell time, of between 2 and 15 minutes, after which it was cooled as rapidly as possible to 100°C, using a mixture of

water and air. Typically the assembly reached the compaction temperature in 4 minutes and cooled in a similar time.

RESULTS AND DISCUSSION

Preliminary experiments suggested the optimum compaction temperature was between around 255°C. Therefore a set of experiments was carried out using a compaction temperature of 255°C and a range of dwell times at the compaction temperature between 2 and 15 minutes. Figure 2 shows the stress-strain curves of these samples and Figure 3 the measurements of Mn for these samples.
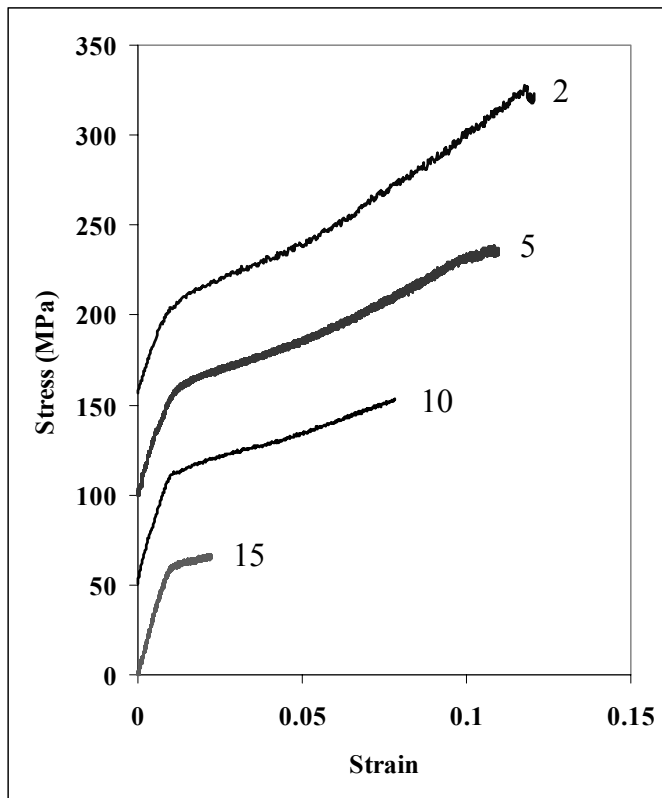
Figure 2: The effect of dwell time on compacted PET sheet properties (the numbers denote the dwell time in minutes)
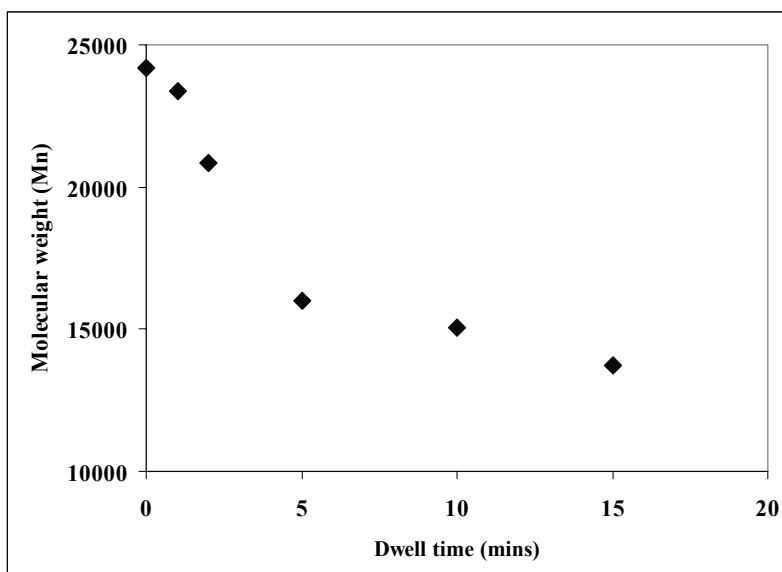
Figure 3: Mn versus dwell time for compacted PET sheets.

The result show a clear decrease in failure stress and failure strain with increasing dwell time at the compaction temperature, and this is linked to a significant fall in the number average molecular weight Mn, from a value of 25,150 g/mol for the original fibres to less than 15,000 g/mol after a dwell time of 15 minutes. The implication of these results is that in order to make good compacted PET samples it is a requirement to keep the assembly at the compaction temperature for the minimum time. It was found that for compaction times of less than 2 minutes, insufficient melting and development of bonding occurred, with the result that the samples were poorly compacted: 2 minutes is therefore considered optimum.

In the next series of experiments, samples were made over a range of temperatures from 253 to 259°C, all using a 2 minute dwell. The aim of this series of experiments was to establish the optimum compaction temperature. Measurements were made of the in-plane tensile modulus and the peel strength and the results are shown in Figure 4.
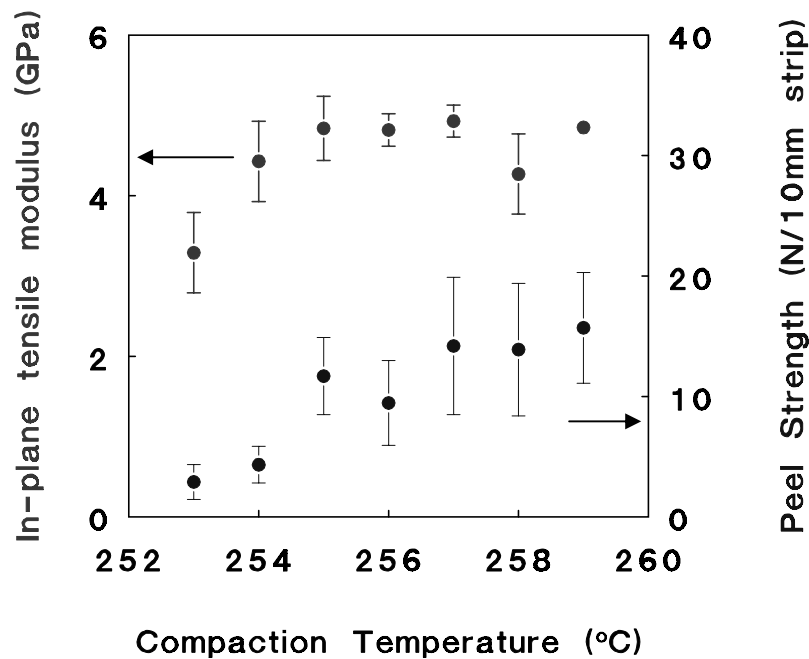

Figure 4: In-plane tensile modulus and peel strength versus compaction temperature

The results show that, in common with previous studies on PP and PE, as the compaction temperature was increased the peel strength, i.e. the level of interlayer bonding developed as a result of melting an increasing percentage of the original oriented phase, also increased. The in-plane modulus meanwhile, increased up to a plateau value of around 5GPa and then stayed at this level between 255 and 259°C. Above 259°C the samples were found to be completely melted and the modulus reverted to that of the original isotropic polymer at around 2.4 GPa. The level of bonding developed over this temperature range, between 255 and 259°C, is the highest so far seen in the compacted composites we have investigated: compacted PP and PE typically showed values of the order of 9N for 10mm wide strip. One can therefore conclude that PET makes a better matrix material for a hot compacted PET composite than polyolefins as a consequence of its higher cohesive strength. This may

be an advantage if the resulting sheets are required to be thermoformed for the chosen application. From the results on Figure 5 we can conclude that the optimum temperature for compaction is 257 ± 2 °C, giving a reasonable processing window for the procedure.

Having established the optimum compaction conditions, more detailed studies were carried out using DSC and DMTA techniques. Measurements of the glass transition temperature of the isotropic, oriented and compacted PET polymer provided confirmation of the ideas developed during the polypropylene studies, of considering the hot compacted sheets as a polymer/polymer composite whose properties depend on a mix of the properties of the constituents. It is well know that the glass transition temperature of PET is raised during the drawing process used to make the oriented filaments, due to changes in chain conformation and crystallinity. During the hot compaction process, a fraction of the skin of these oriented elements is melted, and this material then reverts to the isotropic configuration. Figure 5 shows the glass transition (T_g) of three PET samples, an oriented fibre, a piece of completely melted fibre (taken as equivalent to the 'matrix' material of the hot compacted sheet) and a piece of the hot compacted sheet.
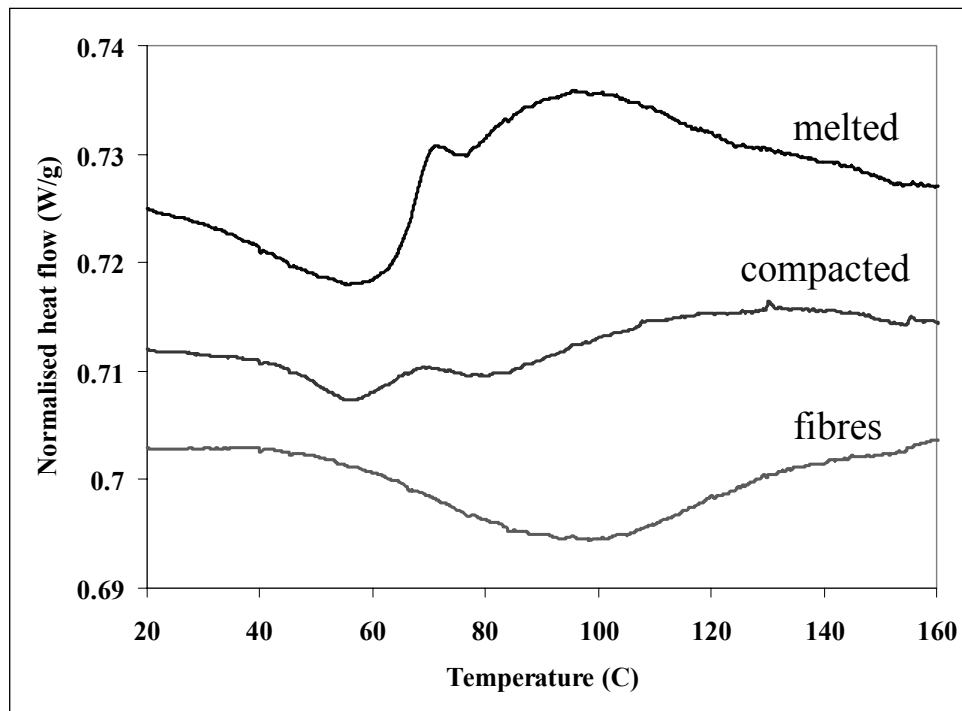

Figure 5

It is seen that the original oriented fibres show a higher T_g compared to the isotropic (or melted) material [120°C and 67°C respectively] and that the compacted sheet shows two peaks, one for the matrix material component [62°C] and one for the remaining oriented fibres [99°C]. The ratio of the specific heats of the two peaks seen in the compacted material, compared to the 100% values, can give a value for the fraction of each phase, which in this case was determined to be 24% matrix material and 74% remaining oriented fibres, which is a typical ratio for optimum hot compacted woven samples. Interestingly the glass transition temperature of the oriented fibre peak in the compacted sheet is lower than that measured for the original

fibres suggesting some shrinkage and morphological changes in the oriented fibres during the compaction procedure.

Another key finding of the PET studies was confirmation of the importance of ductility of the matrix phase. As with the polypropylene work, ductility of the melted and recrystallised matrix phase was found to be promoted by fast cooling after compaction, reducing crystallinity and hence promoting ductility.

Having established the optimum conditions for the compaction of PET, the interest was to assess how the properties compared to two comparative classes of materials: firstly with other PET based materials (isotropic PET and short glass filled PET) and secondly with other compacted, self reinforced polymer sheets, namely polypropylene and polyethylene. Table 2 shows a comparison of selected mechanical properties for compacted PET sheet, isotropic PET and short glass fibre filled PET at a weight fraction of 40%. These two comparative materials were chosen because previous studies on polypropylene have shown that the properties of self reinforced, hot compacted single polymer composites, in general lie between isotropic and glass filled polymers. The comparative values are taken from the MATWEB website (www.matweb.com) and are average values of all commercially available grades of that type. Although the PET polymer used in the three materials may be different, the comparison is still useful.

	Unit	ASTM Standard	Isotropic PET	Compacted PET	Glass/PET 40% w/w
Density	kg/m^3		1320	1400	1570
Tensile Modulus	GPa	D638M	2.7	5.82	11
Tensile Strength	MPa	D638M	55	130	120
Strain to failure	%	D638M	130	11.4	3.2
Heat deflection temperature (1820kPa)	°C	D648	74	108	220
Thermal expansion	x 10^{-6} /°C	D696	79	26.4	14.2
Notched Izod (20°C)	J/m	D256	140	2020	940

Table 2: A comparison of properties of hot compacted PET, isotropic PET and glass filled PET.

The density, tensile modulus, heat deflection temperature, and thermal expansion all lie between the isotropic and glass filled polymer as might be expected. Compacted PET sheet can therefore be seen mainly as an enhanced isotropic polymer, by virtue of the preferred molecular orientation which comes from the original oriented filaments. More interestingly, the tensile strength of the compacted PET sheet is greater than either material and the failure strain lies between the two materials. Consequently, the impact strength, which depends on a combination of the failure strength and the failure strain, is over twice as large as the glass filled PET. The results show that, as for compacted PP sheet, it is the impact strength of compacted sheets that is the most unexpected and outstanding property.

Finally, Table 6 shows a comparison of the properties of optimum sheets of compacted PET, PP and PE (Tensylon tape [12]).

	Unit	ASTM Standard	**PET**	Polypropylene	Polyethylene
Original oriented phase modulus	GPa	D638M	**14**	11	88
Density	kg/m^3		**1400**	910	970
Tensile Modulus	GPa	D638M	**5.82**	5.06	28
Tensile Strength	MPa	D638M	**130**	182	370
Interlaminar peel strength	N/10mm		**18**	9	9
Heat deflection temperature (1820kPa)	°C	D648	**108**	102	132
Thermal expansion	x 10^{-6} /°C	D696	**26.4**	41	-1.5
Notched Izod (20°C)	J/m	D256	**2020**	4760	1340

Table 6: A comparison of typical properties of compacted PET, PE and PP sheets

The in-plane properties, i.e. the tensile modulus and strength, are ranked in order of the properties of the original oriented reinforcements as might be expected. The peel strength of the compacted PET sheets is the highest of the three materials, confirming that if the melted phase remains ductile, then it forms an excellent glue to bind the structure together as a consequence of its higher cohesive strength compared to the polyolefins. Although the impact strength of the compacted PET sheets was not as high as compacted PP, it is still an outstanding value which is higher than most other commercially available materials.

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