Hot Compaction of Woven Poly(ethylene terephthalate) Multifilaments

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ABSTRACT: Here we describe the development of a process, and the resulting mechanical properties, for hot-compacted sheets of woven poly(ethylene terephthalate) (PET) multifilaments. Investigation of the various processing parameters showed that a key aspect was the time spent at the compaction temperature, termed the dwell time. Molecular weight measurements, using 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 dwell time of 2 min was found to be optimum because this gave the required percentage of melted material to bind the structure together, while giving only a small decrease in molecular weight. A combination of techniques, including mechanical tests, differential scanning calorimetry, and scanning electron microscopy, was used to examine the mechanical properties and morphology of the optimum compacted sheets. These tests reinforced the view from previous studies on hot-compacted polypropylene, of hot-compacted sheets as self-reinforced composites, whose behavior is a combination of the properties of the two components, that is, the original oriented multifilaments and the melted and recrystallized matrix. Other key findings from the research included a confirmation of the importance of obtaining high ductility in the melted and recrystallized phases, promoted by using a high molecular weight or by suppressing crystallinity during processing, and the proportionately high-impact performance of hot-compacted sheets, compared with that of other materials. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2223–2233, 2004

Key words: hot compaction; mechanical properties; polyethylene terephthalate

INTRODUCTION

In a number of recent articles we have described the development of a process, termed "hot compaction," for forming novel polymer/polymer composites from highly oriented polymer fibers or tapes. The essence of the process is to take these highly oriented polymers, and choose suitable conditions of temperature and pressure such that a thin skin of each fiber or tape is selectively melted. On cooling, this melted material recrystallizes to form the matrix of the composite and bind the structure together. The resulting hot-compacted composite material is therefore composed of a single, identical, polymeric material, and as such has often been termed "self-reinforced."

The initial studies were carried out on unidirectionally arranged arrays of high-modulus melt-spun polyethylene fibers.[1,2] Morphological studies were able to confirm that selective surface melting of the fibers had occurred and that excellent fiber/matrix adhesion was achieved by virtue of epitaxial crystallization of the molten matrix phase onto and between the oriented fibers. Further studies on unidirectional arrays of gel-spun polyethylene fibers[3] and poly(ethylene terephthalate) (PET) fibers[4] showed similar compaction mechanisms. Most recently the studies have been expanded to examine the hot compaction behavior of commercially available woven polyethylene fibers and tapes.[5,6] Woven cloth was found to give a compacted sheet with a better balance of mechanical properties than that of the highly anisotropic unidirectional arrays originally studied.

Perhaps the most important polymer to be studied has been polypropylene. Hot compaction experiments using cloth woven from oriented polypropylene tapes[7–9] has produced materials that have a unique combination of properties including low density, good mechanical properties, outstanding impact strength even at low temperatures, recyclability, and thermoformability. As a result of this portfolio of properties, hot-compacted polypropylene is now being developed by BP AMOCO, under the trade name CURV™. More fundamental studies on a range of commercially available woven polypropylene cloths,[10,11] including detailed morphological investigations, showed that hot-compacted polypropylene sheet must be considered as a composite, with the properties of the final material depending on the properties of both of the two component phases. The role of the oriented rein-

TABLE I
Details of the PET Fibers[a]

Number-average molecular weight M_n (g/mol)	Filament linear density	Filament initial modulus (GPa)	Filament breaking strength (MPa)	Filament failure strain (%)
25,150 ± 500	1100 dtex	14	1000	19

[a] Density = 1400 kg/m³.

forcing fiber or tape is to provide high stiffness and strength, whereas the matrix acts as a binder but can contribute significantly to the compacted sheet modulus. Unusually for a composite, the failure strain of the oriented reinforcement can be higher than that of the melted and recrystallized matrix phases. It is therefore crucial to have as high a strain to failure for the matrix phase as possible, to allow the composite to remain integral up to the failure point of the reinforcement. Higher molecular weight and lower crystallinity (which was produced using a faster cooling rate) was found to help promote the ductility of the matrix phase.

In this article we describe recent experiments to investigate the hot compaction of poly(ethylene terephthalate). PET is of interest because it a commercially available oriented polymer, which has the potential to show better mechanical and temperature performance than that of a drawn polypropylene fiber or tape. 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 those of the best hot-compacted polypropylene sheets.

EXPERIMENTAL

The details of the woven PET cloth used in this investigation are shown in Table I: the cloth was a plain weave construction (Fig. 1; the warp runs from the bottom left to the top right) composed of 1100 dtex filament bundles (0.21 mm diameter), with a number-average molecular weight (M_n) for the base polymer of 25,150 kg/mol. The M_n was measured using the intrinsic viscosity technique as described in the next section.

Sample preparation

A crucial aspect of the hot compaction of PET is the requirement to first keep the assembly at the compaction temperature for the minimum possible time to inhibit hydrolytic degradation and, second, to cool the sample rapidly after compaction to promote ductility in the melted fraction. To achieve these goals, it proved necessary to develop a new variant of the
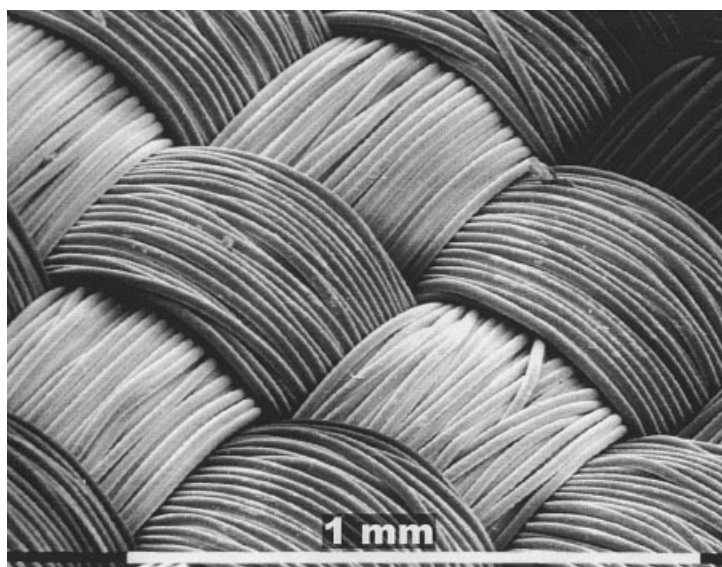

Figure 1 SEM micrograph of the woven PET cloth.

standard batch technique described in previously published work on the hot compaction of polypropylene[8,12] and polyethylene,[1,5,13] where the compaction assembly was contained inside a matched metal mold. 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 that of a thick metal mold assembly. The compaction procedure was therefore as follows. First, the layers of woven PET cloth (175 mm^2) were assembled between brass plates, with outer layers of PTFE release film and soft aluminum 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 in a vacuum oven set at 80°C overnight (16 h) 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 2.8 MPa (400 psi) 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 min, 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 min and cooled in a similar time.

Molecular weight determination: intrinsic viscosity

The molecular weight of the materials involved in this study was measured using a Ubbelohde dilution viscometer (Cannon–Ubbelohde, State College, PA) suspended in a water bath at 25°C. A 0.125 mg portion of each sample was dissolved in 25 mg 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 compared against that of the pure solvent. Three further dilutions allowed the intrinsic viscosity to be determined by extrapolating to zero concentration. The viscosity-average molecular weight M_v, equivalent to 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, M_n is the viscosity-average molecular weight, and k and α are the Mark–Houwink parameters. For PET/TFA these values are given by Moore and Sanderson[14] as 1.4×10^{-3} and 0.64 for k and α, respectively, at 25°C.

Differential scanning calorimetry (DSC)

DSC has proved very useful in previous studies on other materials, both for determining the likely compaction temperature range and for examining the structure of materials after compaction. Melting studies, using a Perkin–Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) were carried out on both the original fibers, on compacted sheets, and on sheets of completely melted material to understand the changes in crystalline structure as a result of the various processing regimes. All scans were carried out at a scanning rate of 10°C/min.

Mechanical tests

A variety of physical tests were carried out to assess the mechanical properties of the compacted PET sheets; where possible these were carried out to the appropriate ASTM testing standard. The tests had two main functions: (1) tensile and peel tests were used to establish the optimum processing conditions required to make good compacted samples; and (2) once the optimum conditions were established, a wider range of tests was used to establish a comparison between the properties of compacted PET sheets and comparative materials.

Tensile stress–strain behavior (ASTM D638M) was measured using an RDP-Howden (Lemington Spa, Warwicks, UK) servomechanical test machine using a Messphysik video-extensometer to measure sample strains. The bonding developed during compaction was measured using a T-peel test (according to ASTM D1876). Samples for this test were made by placing a 10-mm-wide strip of thin aluminum foil between the central two layers of cloth in the compaction assembly. The width of the peel samples was 10 mm, so the results are presented as a peel load/10 mm. The samples used for the tensile and peel tests were of the order of 0.7 mm thick, and the peel tests were carried out at a displacement rate of 80 mm/min. Dynamic mechanical tests were carried out using a Rheometrics Solids Analyzer (RSA II) over a temperature range 20–150°C.

The impact strength of the compacted PET sheets was measured using an Izod testing geometry (ASTM D256): samples for this test were 5 mm thick. The heat deflection temperature (ASTM D648) and thermal expansion coefficient (ASTM D696) were also measured on 5-mm-thick samples.

Peel fracture surface analysis

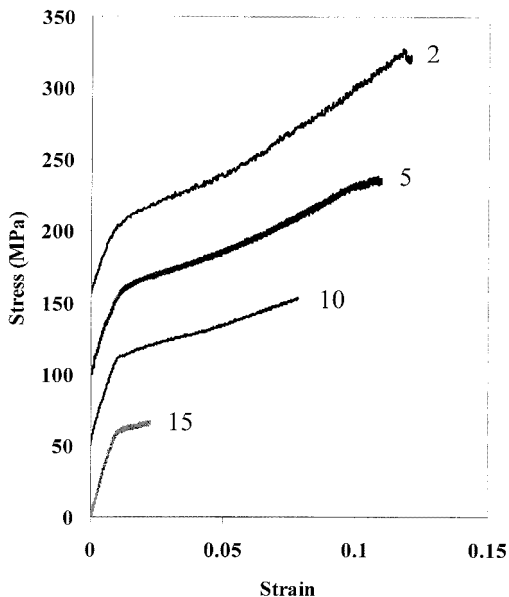The fracture surfaces of a number of tested peel samples were examined using a scanning electron micro-

Figure 2 Effect of dwell time on compacted PET sheet properties.

Figure 4 Plot of ln(half-life) versus ln(degradation temperature).

scope. A picture of the original woven PET cloth was also taken to aid interpretation of the details on the fracture surfaces. To obtain these pictures, the samples were coated with gold and examined under a Philips 515 scanning electron microscope (SEM; Philips, The Netherlands). Specimens were tilted by 45° to improve contrast and to give a good three-dimensional impression.

RESULTS AND DISCUSSION

Effects of hydrolytic degradation

Preliminary DSC and tensile experiments suggested that the optimum temperature for compaction was between 255 and 258°C. Consequently, a preliminary
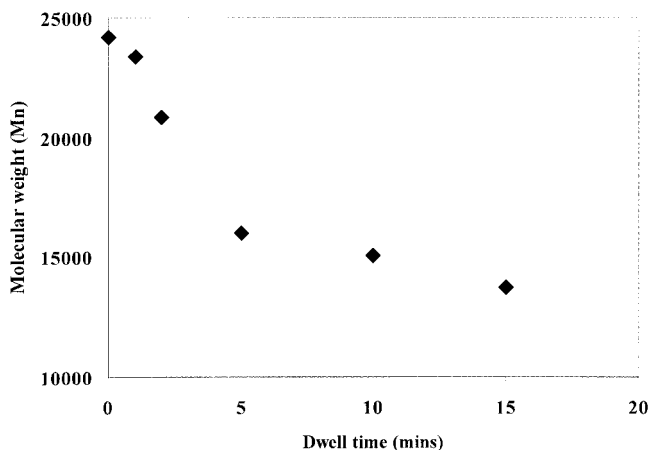
series of experiments was carried out using a compaction temperature of 255°C, but using various dwell times at the compaction temperature. Figure 2 shows typical in-plane stress–strain curves taken from samples compacted using dwell times of 2, 5, 10, and 15 min: the curves have been shifted up the y-axis to make the differences more apparent. It is seen that with increasing dwell time the samples become more brittle, with a significant decrease in the failure stress and failure strain. An obvious reason for this, which is well known from previous work both in this department[15] and from other workers on PET,[16–18] is the process of hydrolytic degradation, which can occur at elevated temperatures.

To establish whether this was the cause of the measured embrittlement, measurements were made of M_n values for samples made at the various dwell times. The results of this determination are shown in Figure 3. The results show clearly that the molecular weight falls rapidly from a value of 25,150 g/mol for the
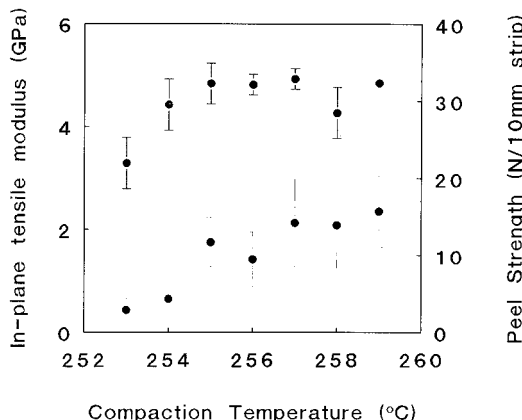

Figure 3 M_n versus dwell time for compacted PET sheets.

Figure 5 In-plane tensile modulus (upper results) and peel strength (lower results) versus compaction temperature.
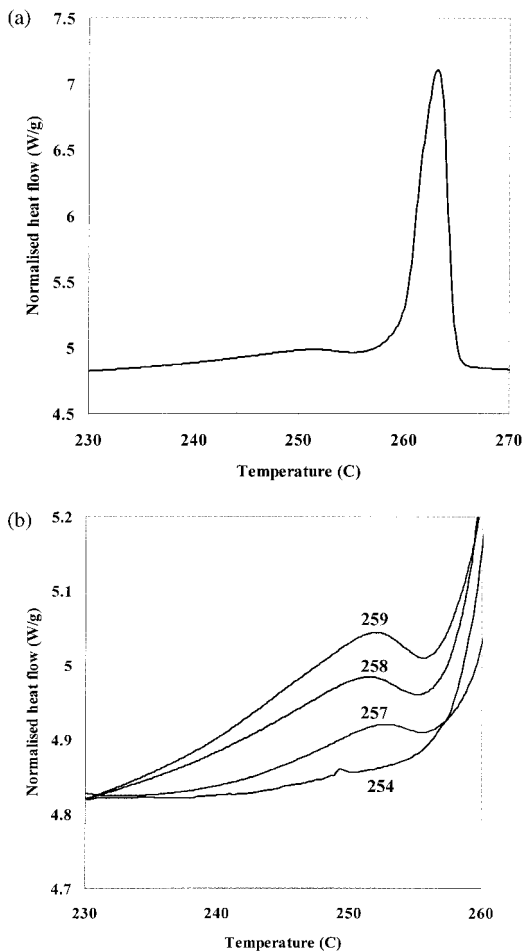
Figure 6 DSC melting endotherms of compacted PET sheets: (a) typical DSC of compacted sheet made at 258°C; (b) close-up of lower melting peak.

original fibers to less than 15,000 g/mol after a 15-min dwell at the compaction temperature. Plotting the values of M_n versus the log of the dwell time gave a value for the half-life, or the time for the molecular weight to
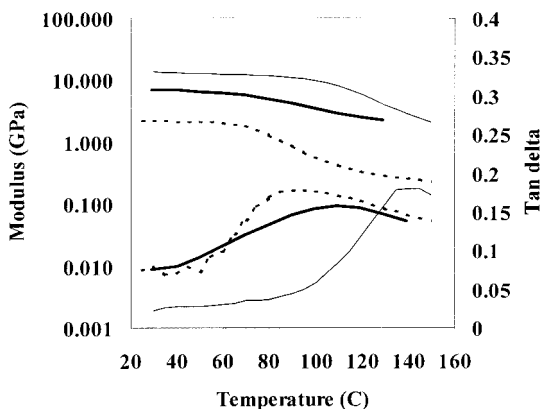

Figure 7 DMTA traces for original PET fiber (—), optimum compacted PET sheet (257°C) (■), and melted "matrix" (- - -).
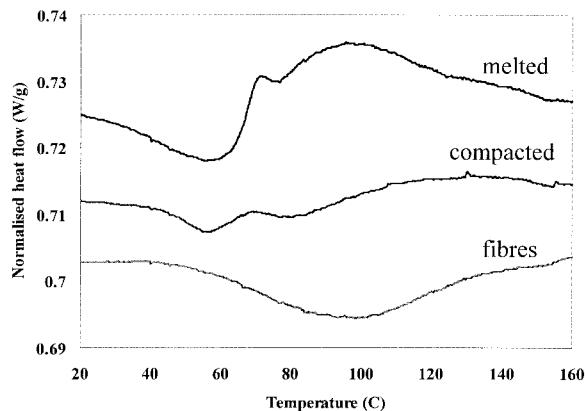

Figure 8 Glass transitions of various PET materials.

drop by a half, as 21 min. It is useful to compare this value of the half-life, with results determined in a previous study carried out in this department by Zhang and Ward.[15] In previous studies, the kinetics of hydrolytic degradation were investigated at temperatures between 120 and 160°C, in 100% humidity. Figure 4 shows a log–log plot of the half-lives derived from both the previous study (■) and the current work (♦) plotted against the degradation temperature. The current result, at a temperature of 255°C, fits well with the trend from the previous study, and suggests a very similar mechanism but just enhanced by the higher temperatures required for compaction.

The implication of these results is that 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 min, insufficient melting and development of bonding occurred, with the result that the samples were poorly compacted. As an alternative strategy, samples were made by first drying the cloth overnight at 80°C, to remove any trapped water; 80°C was chosen as the drying temperature because at higher temperatures significant filament shrinkage was measured, with the resulting loss of molecular orientation and filament mechanical properties. After drying, the assembly was compacted as normal, using a temper-

TABLE II
Change in Specific Heat and Glass-Transition Temperatures of the Various PET Materials

Material	ΔC_p (J/g^{-1}/°C^{-1})	T_g (°C)
Melted fiber	0.075	66.5
Original fiber	0.046	~ 120
Compacted sheet lower peak	0.018	62
Compacted sheet upper peak	0.035	99
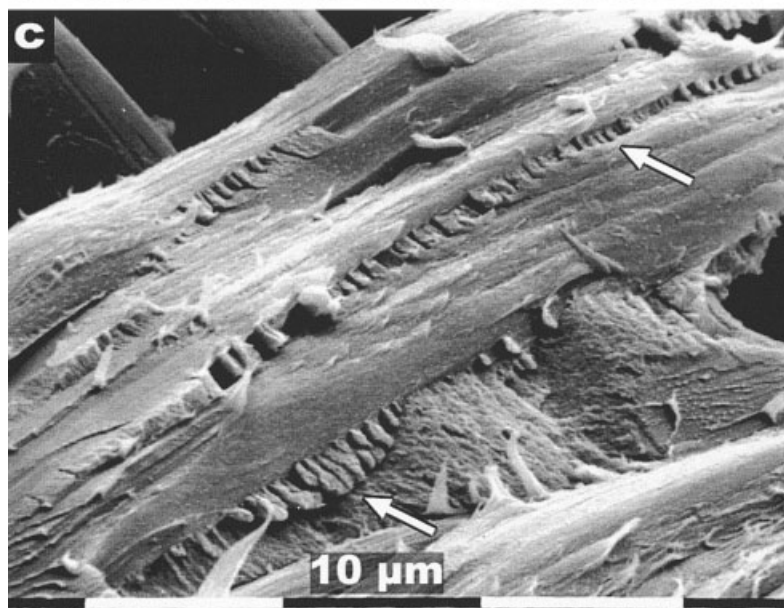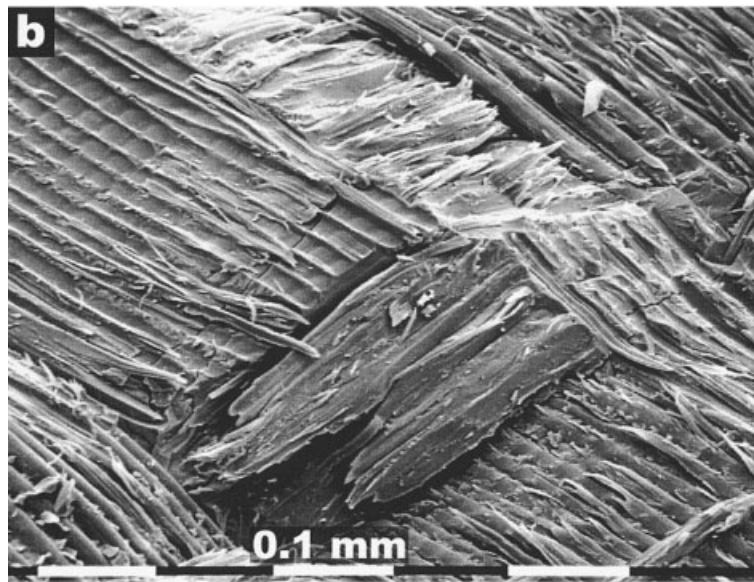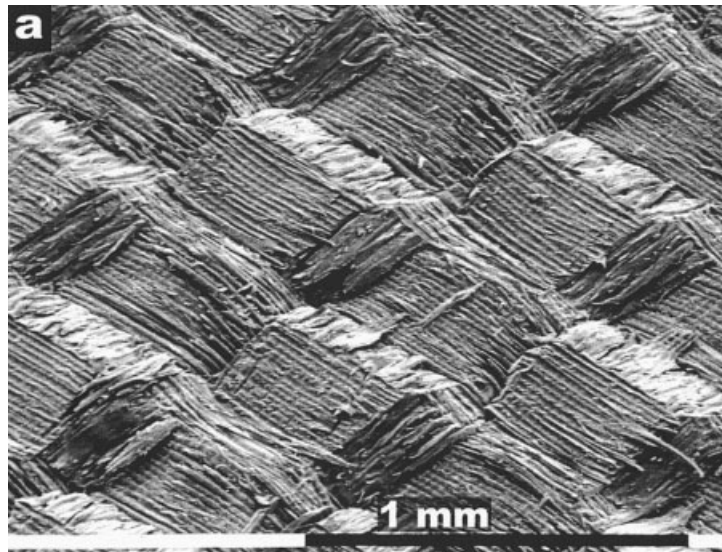
ature of 255°C and a dwell time of 5 min. Mechanical tests showed a similar failure strength and strain to that seen for the 2-min dwelled sample that had not been dried. Subsequent molecular weight measurements confirmed this result with a value for M_n of 22,970 g/mol, which was much higher than the 5-min dwelled sample that had not been dried, which gave a value for M_n of 15,209 g/mol.

There are therefore two choices to make compacted PET samples with minimal hydrolytic degradation: either carry out the compaction processes in the minimum time, or dry the PET cloth beforehand, where a little more license with the compaction time is available. Because the former process lends itself more easily to scale-up and commercialization, this is the procedure used for the rest of the results presented in this article (i.e., a 2-min dwell).

Establishing the optimum compaction conditions

In the next series of experiments, samples were made over a range of temperatures from 253 to 259°C, all using a 2-min 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 5. 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 to a plateau value of about 5 GPa and then remained 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 9 N/10 mm. 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.

DSC melting endotherms were also measured on this range of samples, made between 253 and 259°C. The samples all showed a DSC trace characteristic of a compacted sheet: a typical example is shown in Figure 6(a), in this case for a sample compacted at 258°C. The upper, larger peak is associated with the remaining fraction of the original oriented filaments, whereas the lower, smaller, and broader peak is associated with the melted and recrystallized "matrix" phase produced during compaction. The reason for the lower melting peak of the matrix phase could be attributable to reverting to smaller-size lamellae on melting, or possibly an effect of the different levels of orientation (i.e., constraint) in the two phases. The lower peak is smaller than seen previously with PE and PP compacted materials, suggesting a lower crystallinity for the matrix phase. This could be a palpable advantage because, as will be seen shortly, it is an advantage for the matrix phase to be ductile, and this is likely to be enhanced if the crystallinity is low. Figure 6(b) shows a comparison of the size of the lower peak from samples compacted at different temperatures and confirms the increase in the amount of the "matrix" phase with increasing compaction temperature.

DSC measurements have often been used in our previous work to determine the fraction of the two phases in a compacted composite (i.e., the original oriented "reinforcement" phase and the melted and recrystallized "matrix" phase). What this actually calculates is the fraction of the crystalline portion of each phase after the compaction procedure has been carried out. Although there are potential doubts over recrystallization of PET during the DSC test itself, we can still do this calculation here. As an example, for the optimum sample made at 257°C, this would predict a fraction of 82% for the original oriented phase, and therefore a fraction of 18% for the melted matrix phase.

Dynamic mechanical tests (DMTA) were used to examine the behavior of the various materials. Figure 7 shows results of dynamic tests carried out at a frequency of 1 Hz on the original PET fibers (thin line), the melted matrix material (dotted line), and the optimum compacted sheet (solid line). To examine the properties of the melted "matrix," films were made by melting out the filaments completely, and then cooling under the same conditions as used to make the compacted PET sheets. In Figure 7, the top three lines show the relevant modulus values and the three lower lines the values of tan δ. As would be expected, the compacted sheet modulus lies between the fiber and

Figure 9 SEM micrographs of peel fracture surfaces: (a) low-magnification picture of a typical peel fracture surface of compacted PET; (b) intermediate-magnification picture of a peel fracture surface; (c) high-magnification picture of a peel fracture surface showing evidence of epitaxial recrystallization of the melted matrix phase (as shown by the white arrows).

matrix values. Similarly the peak in tan δ (often used as a measure of the glass-transition temperature T_g) of the compacted sheet lies between that of the fibers and matrix phases: interestingly, the compacted sheet T_g is significantly lower than that of the original fibers. It is well known[19] that during the orientation of PET, major structural changes occur in the amorphous phase. As well as an increase in the amorphous orientation, there is also a change of the predominant chain configuration, from *gauche* to *trans*, which affects the glass transition of the main chain. Therefore the oriented filaments and the melted "matrix" should show a different T_g, and the compacted PET sheet should show some combination of these two transitions.

Another way to assess the glass transition of the three materials is to use DSC. Figure 8 shows typical examples of DSC endotherms around the glass transition for the three materials, and the numerical results are shown in Table II. Samples of completely melted material showed a sharp transition characteristic of isotropic PET, of 66.5°C: the change of specific heat ΔC_p through the transition was 0.075 J/g/°C. The oriented filaments, on the other hand, had the expected higher transition of about 120°C with a ΔC_p of 0.046 J/g/°C. The compacted sheet, chosen as the optimum sample made at 257°C, showed both the low and high transitions, with a sharp one at 62°C and a broader one at about 100°C. The decrease in T_g of the compacted sheet, compared to that of the original fibers, mirrors the DMTA results shown in Figure 7 and described above, suggesting that structural changes could be occurring during the compaction procedure. Taking the ratios of the changes in specific heat would give the optimum compacted sheet as composed of 24% of the melted and recrystallized matrix and 76% of the oriented reinforcement. Within the errors of the two techniques, this is a very similar fraction to that determined above by the DSC melting studies and to that seen in all the other optimum compacted materials so far studied.

Both the DSC and DMTA results reinforce the view of the compacted sheet as a composite whose properties depend on a combination of those of the oriented fiber and melted matrix phases.

Fractography

SEM micrographs were taken of a typical peel sample to be able to look directly at the morphology of the compacted PET samples, rather than indirectly as with DSC and mechanical tests. In previous studies on PE and PP, etched micrographs have been very successful in showing the two phases of the compacted composite materials. However, in the previous work on unidirectionally aligned PET,[4] etched micrographs showed no evidence of the melted and recrystallized phases, only holes in the structure where it had been.

It appeared that the melted matrix had been much more severely attacked by the etchant (a permanganic reagent) than in PE or PP, perhaps a further indication of the lower crystallinity of this phase as indicated earlier. Therefore it was decided to use direct fracture surface analysis to examine the microstructure.

As shown earlier in Figure 1, the original cloth was formed of woven bundles of oriented multifilaments. Figure 9 shows some examples of typical peel fracture surfaces, which contain information on both the compacted PET sheet microstructure and the fracture event itself. Figure 9(a) shows a low-magnification picture of a peel fracture surface in the same orientation as Figure 1 with the warp bundles running from bottom left to top right. Interestingly, the way that the two layers of cloth were pressed together on compaction controls the view of the microstructure seen. Consequently, the exposed areas of the warp bundles show sockets of melted "matrix" material that run at 90° to the fibers underneath. Similarly the exposed sections of the weft bundles, which run from top left to bottom right, show evidence of the fibers from the other half of the fracture surface, again at 90° to the filaments underneath. A higher-magnification picture [Fig. 9(b)] of the center of this region shows these effects more clearly. In particular, the bundle at the top left, which is a warp bundle running from bottom left to top right, clearly shows the sockets of matrix material at 90° to this direction. This fracture surface shows regions of both deformed and fractured melted matrix material, and damage within the fibers themselves (top right) reflecting the good adhesion (stress transfer) between the two phases. In addition, the replication of the opposing mating layer reflects good wetting of the matrix phase.

As described above, detailed investigation of the recrystallized lamellar morphology is more difficult in PET because it is more easily attacked by the etchants. However, the peel fracture surfaces did show indications of a similar morphology to PE and PP, that is, epitaxial recrystallization of the matrix phase onto the remaining oriented fiber backbone. Figure 9(c) shows a high-magnification micrograph of a number of filaments running from bottom left to top right. The fractured material around and between the fibers has the appearance of epitaxially recrystallized material. Although not definitive, this information suggests a compaction morphology in PET similar to that in hot-compacted PE and PP.

Effect of cooling rate on matrix properties

From the mechanical measurements and morphological pictures, it is clear that as for compacted PP, compacted PET can be envisaged as a single-polymer composite, where the reinforcing phase is the oriented filament bundles and the matrix is the melted and
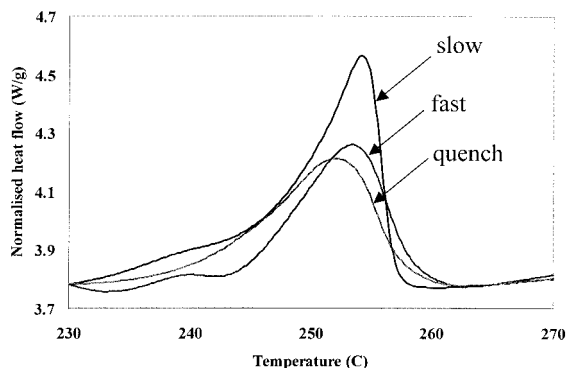
Figure 10 Melting behavior of melted PET films with different cooling rates.

Figure 11 Mechanical properties of melted PET films.

recrystallized fraction. As with any composite, it is important that the matrix remains coherent up to the point where the reinforcement fails. For this reason, it has proved very important to study ways in which the ductility of the matrix phase is affected. The most recent PP studies[10,11] suggested molecular weight and crystallinity (affected by the cooling rate) as being very important contributory effects. The results of using different dwell times described above, and the effect on the matrix molecular weight, have already highlighted the importance of this first factor. In this section the effect of cooling rate on matrix properties is investigated.
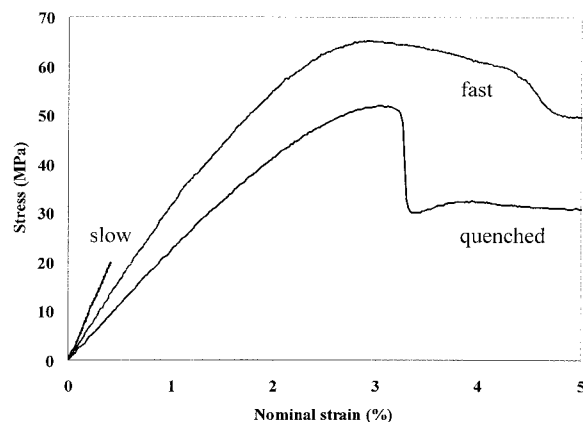
The effect of cooling rate on matrix crystallinity, and hence ductility, was investigated by making sheets by completely melting out the woven PET cloth at 270°C: the sample was left at the melting temperature for the same time as the compacted sheets, which was 2 min, to minimize hydrolytic degradation. After melting, the samples were either quenched in water, cooled at the same rate used to make the optimum compaction samples (fastest possible on a heated press of $\sim$ 30°C/min), for slow cooled, where the hot press was switched off after the 2-min dwell time.

The DSC results from the melted samples (Fig. 10 and Table III) show the expected results; that is, the faster the cooling rate, the lower the resulting crystal-

linity. In addition the DSC endotherms show that the faster the cooling rate, the lower the peak melting temperature and, with inference, the smaller the crystal size. Taking the value for the enthalpy of melting of PET as 140 J/g,[20] gives values for the crystallinity of 32, 23, and 21% for the slow cooled, fast press cooled, and quenched samples, respectively. The biggest difference is seen between the slow cooled and the other two samples, with the fast press cooled sample closer to the quenched sample. For comparison, the melting enthalpy of the original filaments was 44 J/g, giving a crystallinity of the original oriented phase of 42%, showing that even the slow cooled melt samples do not revert to the crystallinity of the starting material.

Mechanical measurements were carried out on the various melted films, and the results are shown in Figure 11 and Table IV. The quenched samples were ductile, showing stable drawing behavior and a rapid decrease in load as a neck region was formed. Because of the appearance of a neck in these samples, the strain in the gauge length was determined from the nominal testing machine displacement. The fast hot press cooled sample, which was hoped to be representative of the melted matrix found in a compacted sheet, showed pseudoductile failure, with a broad yield

TABLE III
Enthalpy of Melting and Percentage Crystallinity from Various PET Materials

PET material	Enthalpy of melting ΔH^a (J/g)	Percentage crystallinity
Slow cooled	45	32
Fast cooled	32	23
Quenched	30	21
Piece from a compacted sample	29	20
Original fibre	44	42

^{a} ΔH for 100% crystalline PET = 140 J/g.

TABLE IV
Properties of Melted Films Made at Various Cooling Rates^a

Property	Slow cool	Fastest hot press cool	Quench cool
Young's modulus (GPa)	4.1 ± 0.1	2.9 ± 0.1	2.3 ± 0.4
Maximum stress (MPa)	16 ± 5(B)	66 ± 1(Y)	50 ± 2(Y)
Strain at max stress (%)	0.4 ± 0.1	3.1 ± 0.1	3.3 ± 0.1

^{a} (B) brittle failure stress; (Y) ductile failure–yield stress.

TABLE V
Comparison of Properties of Hot Compacted PET, Isotropic PET, and Glass-Filled PET

Property	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 (1820 kPa)	°C	D648	74	108	220
Thermal expansion	$\times 10^{-6}$/°C	D696	79	26.4	14.2
Notched Izod (20°C)	J/m	D256	140	2020	940

point followed by eventual failure of the sample. This type of failure is often termed necking-rupture.[21,22] The fastest hot press cooled sample showed an increased modulus and yield strength over those of the quenched sample.

The third melted material, the slow cooled sample, although showing a further significant increase in the modulus, also showed brittle failure at a very low stress. Although some of this embrittlement is attributed to increased crystallinity, as shown in Figure 10 and Table III, it must also be acknowledged that the increased cooling time will result in the sample spending longer at an elevated temperature, with an associated increase in hydrolytic degradation. Intrinsic viscosity measurements on the slow cooled film confirmed this, with a value of M_n of 18,750 g/mol compared to the original fiber value of 25,150 g/mol, which is a significant decrease. Therefore, for the slow cooled sample, it is impossible at the present time to separate the effects of increased crystallinity and hydrolytic degradation on mechanical properties. However, we can conclude that fast cooling is a definite advantage in promoting matrix ductility. Similarly, the results suggest that at practically achievable cooling rates, matrix ductility can also be achieved.

As a cautionary note, it must be acknowledged that the mechanical tests on these thin films, under a state of plane stress, are unlikely to be exactly representative of the melted material in the compacted composite, which will be under conditions of plane strain. Because plane strain conditions will suppress ductility, it is even more important to achieve rapid cooling after compaction. Future experiments will include tests on thicker samples of the isotropic polymer, to assess ductility under plane strain conditions.

Comparison of the mechanical properties of optimum PET samples with other materials

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: first with other PET-based materials (isotropic PET and short glass fiber–filled PET) and, second,

with other compacted, self-reinforced polymer sheets of polypropylene and polyethylene.

Table V shows a comparison of selected mechanical properties for compacted PET sheet, isotropic PET, and short glass fiber–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 generally 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. Of course, the actual type of PET polymer used in the three materials may be different, but the comparison is still useful. 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 reason of the preferred molecular orientation that comes from the original oriented filaments. More interestingly, the tensile strength of the compacted PET sheet is greater than that of either material and the failure strain lies between that of each of 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 that of the glass-filled PET. The results show that, as for the compacted PP sheet, it is the impact strength of compacted sheets that is the most unexpected and outstanding property.

Finally, Table VI shows a comparison of the properties of compacted PET, PP, and PE 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 that of the polyolefins. Although the impact strength of the compacted PET sheets was not as high as that of

TABLE VI
Comparison of Typical Properties of Compacted PET, PP, and PE Sheets

Property	Unit	ASTM standard	PET	PP	PE
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/10 mm		18	9	9
Heat deflection temperature (1820 kPa)	°C	D648	108	102	132
Thermal expansion	$\times 10^{-6}$/°C	D696	26.4	41	−1.5
Notched Izod (20°C)	J/m	D256	2020	4760	1340

compacted PP, it is still an outstanding value—higher than that of most other commercially available materials.

CONCLUSIONS

Here we have described an investigation into the hot compaction behavior of woven oriented PET multifilaments. A key finding was that, although hydrolytic degradation can occur rapidly at the temperatures required for the hot compaction process, excellent samples can be made either by using a short dwell time of about 2 min (keeping hydrolytic degradation to a minimum) or by drying first, when a slightly longer dwell time of about 5 min could be used. The processing window for hot compaction, where an optimum combination of properties was obtained, was determined to be quite reasonable at around 257 ± 2°C. The morphology of the optimum hot-compacted PET sheets, determined from an investigation of peel fracture surfaces, was found to be similar to that seen previously for compacted polyethylene and polypropylene samples, that is, a melted phase epitaxially crystallized onto the remaining oriented phase.

DSC and DMTA measurements showed that hot-compacted PET should be considered as a composite material whose behavior depends on both the oriented phase and the melted and recrystallized phase. Mechanical tests showed that matrix ductility is very important for good compacted sheet properties and that this can be achieved by using and retaining a high molecular weight for the original polymer, and by fast cooling after compaction to suppress crystallization of the melted phase. As a final conclusion, melted PET was found to be a very good "matrix" for the hot-compacted composite giving a good suite of mechanical properties including excellent impact strength.

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