

Hot Compaction of Polyethylene Naphthalate

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ABSTRACT: In this article, we describe the production of single polymer composites from polyethylene naphthalate (PEN) multifilaments by using the hot compaction process. In this process, developed at Leeds University, highly oriented tapes or fibers are processed at a critical temperature such that a small fraction of the surface of each oriented element is melted, which on cooling recrystallizes to form the matrix of the composite. This process is, therefore, a way to produce novel high-volume fraction polymer/polymer composites where the two phases are chemically the same material. A variety of experimental techniques, including mechanical tests and differential scanning calorimetry, were used to examine the mechanical properties and morphology of the compacted PEN sheets. Bidirectional (0/90) samples were made at a range of compaction temperatures chosen to span the melting range of the PEN multifilaments (268–276°C). Measurement of the mechanical properties of these samples, specifically the in-plane modulus and strength, allowed the optimum compaction temperature to be ascertained (~ 271°C), and hence, the optimum mechanical properties. The optimum compacted PEN sheets were found to

have an initial modulus close to 10 GPa and a strength of just over 200 MPa. The glass transition temperature of the optimum compacted sheets was measured to be 150°C, nearly 40°C higher than compacted poly(ethylene terephthalate) (PET) sheets. In previous work on polypropylene and PET hot compacted materials, it proved instructive to envisage these materials as a composite where the original oriented multifilaments are regarded as the reinforcing phase, and the melted and recrystallized material are regarded as the matrix phase. Dynamic mechanical bending tests (DMTA) were used here to confirm this for PEN. DMTA tests were carried out on the original fibers and on a sample of completely melted material to determine the fiber and matrix properties, respectively. The composite properties were then predicted by using a simple rule of mixtures and this was found to be in excellent agreement with the magnitude and measured temperature dependence of the hot compacted PEN material. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 796–802, 2004

Key words: hot compaction; polyethylene; naphthalate

INTRODUCTION

In a number of previous articles,^{1–11} we have described how the hot compaction process can be used to produce novel single polymer/polymer composites from highly oriented fibers and tapes (for a review see ref. 12). The essence of the process is to take these highly oriented elements 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.

Although we have found that the hot compaction process is applicable to a number of different thermoplastic polymers, including polyethylene, polypro-

pylene (PP), and poly(ethylene terephthalate) (PET), the commercial developments have focused primarily on PP. Hot compacted PP sheets were found to have a good combination of properties including low density, satisfactory stiffness and strength, and outstanding impact strength even at low temperatures. However, the stiffness and dimensional stability fall quite rapidly as the temperature is increased above room temperature, and the creep increases with increasing temperature, so other polymers have recently been under investigation.

In a recent article, we described the development of a process, and the resulting mechanical properties, for producing hot compacted sheets of woven PET multifilaments, building on the original work on unidirectionally aligned fibers.⁴ A study of the various processing parameters showed that a key feature was the time spent at the compaction temperature, termed the dwell time. Molecular weight measurements 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

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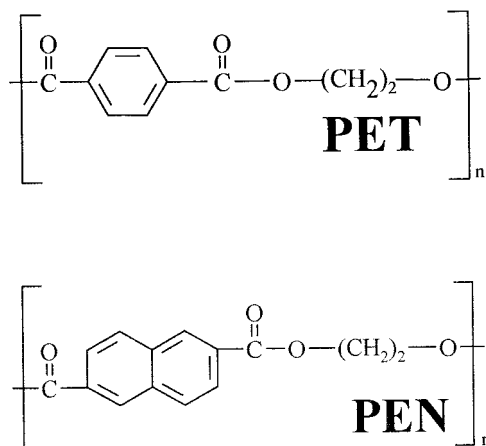


Figure 1 Chemical structures of the repeat unit for poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN).

found to be optimum, as this gave the required percentage of melted material to bind the structure together, while giving only a small decrease in molecular weight. The mechanical properties of the optimum compacted PET sheets showed that PET had roughly comparable mechanical properties to compacted PP at room temperature (+20°C) and at +120°C, but much better properties at temperatures between these limits, offering the potential of improved creep performance in this range. The mechanical tests also showed that compacted PET sheets had a more linear stress-strain curve compared to PP so that at 2% strain PET had almost twice the stiffness of PP: in addition, compacted PET also had a lower thermal expansion than compacted PP.

Polyethylene naphthalate (PEN) has the potential for an even greater improvement in performance because oriented fibers can be produced with a significantly higher stiffness compared to PET¹³ and PEN also has a much higher glass transition temperature (T_g). In addition, previous work by one of the au-

thors¹⁴ has shown that PEN has improved hydrolytic stability compared to PET because of a combination of lower water absorption and lower ester linkage concentration. As described above, hydrolytic degradation was found to be a key issue in the hot compaction of PET, so improvement in this area would be a distinct advantage. For this combination of reasons, we have carried out a study to assess the potential of hot compacted PEN. Sheets were manufactured by compacting bidirectional arrangements of fibers over a range of temperatures around the melting range. Tensile tests were used to determine the mechanical properties of the samples made at various temperatures to determine the optimum processing conditions. Differential scanning calorimetry was used to determine the percentage of the original oriented fibers lost during the process, the fraction of matrix material produced, and any changes to the morphology as a result of the process.

EXPERIMENTAL

Material details and sample production

Figure 1 shows the repeat unit for PEN in comparison with PET. It is seen that the only difference in the structure is the extra phenylene ring in PEN. Table I shows typical properties of both isotropic and oriented PEN, again in comparison with PET. PEN has a similar density to PET but a significantly increased T_g because of the presence of the naphthalene linkage in the PEN backbone. The melting temperature is higher for PEN and the thermal expansion is significantly lower. For the oriented materials, it is seen that both the T_g and the crystallinity is increased.

The PEN fiber used in these studies was supplied by KOSA GmbH (Bobingen, Germany) in the form of a multifilament bundle of weight 1100 g/denier. The most commonly used arrangement of fibers for compaction experiments is a woven cloth, as this results in the compacted sheet having a balance of properties in

TABLE I
A Comparison of the Properties of PEN and PET Materials

	PEN	PET
<i>Isotropic polymer (matrix)</i>		
Density (kg/m ³)	1360	1320
Glass transition temperature (°C)	120–135	67
Melting temperature (°C)	274	256
Crystallinity (fast cooled)	35	23
Tensile modulus (20°C) (GPa)	3.3	2.7
Thermal expansion ($\times 10^{-6}$ K ⁻¹)	44	80
<i>Oriented fibers (reinforcement)</i>		
Glass transition temperature (°C)	160	120
Crystallinity	50	40
Tensile modulus (20°C) (GPa)	23–30	14
Tensile strength (20°C) (MPa)	Up to 1.2 GPa	Up to 1 GPa

the two in-plane axes. Because only continuous filaments were available for PEN, a new technique was developed for producing bidirectional sheets, where the fibers were wound around a metal plate. The fibers were wound in both directions to give a 0/90 lay-up: the winding procedure was in the order 0, 90, 90, and 0 to give a symmetric and balanced lay-up. A thermocouple was placed in the center of the fiber lay-up to allow the process temperature to be accurately monitored. Once produced, the fiber assembly was placed between metal plates and then transferred into a hot press set at the desired compaction temperature, and a pressure of 350 psi was applied. The temperature of the assembly was monitored and after reaching the desired temperature it was left to dwell for 2 min, after which the press was rapidly cooled by using water: a dwell time of 2 min was considered as optimum based on the previous PET studies. Samples were made by using a range of compaction temperatures between 268 and 276°C. A single sample was made by using a dwell time of 10 min, at the optimum compaction conditions, to assess hydrolytic degradation.

Mechanical tests

The mechanical properties of the compacted PEN samples, specifically the in-plane modulus and strength, were measured following the guidelines of the appropriate ASTM testing standard, which for tensile testing is ASTM D638. The tests were carried out by using an RDP Howden servomechanical machine and the sample strain was measured by using a Messphysik video extensometer. The tests were carried out at a nominal strain rate of $2 \times 10^{-3} \text{ s}^{-1}$.

Differential scanning calorimetry (DSC)

A key issue with hot compaction studies is always the melting behavior of both the original oriented fibers and the final compacted sheet. In this work, we used a Perkin-Elmer DSC-7 to examine the melting behavior of the various materials using a scanning rate of 10°C/min.

Dynamic mechanical analysis (DMTA)

As shown in Table I, an important advantage of PEN over PET is the higher T_g of the former. To assess this important property, and to examine the relationship of modulus with temperature, DMTA was used. The measurements were carried out by using a Rheometric Solids Analyzer (RSAII) using a sinusoidal strain of $\pm 0.05\%$ at a frequency of 1 Hz.

RESULTS

Melting behavior and mechanical tests

Before proceeding with the hot compaction experiments, it was first necessary to ascertain the melting

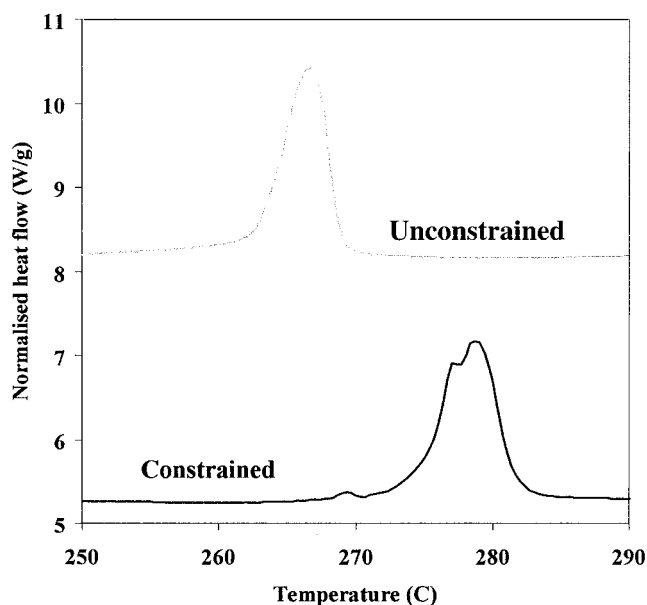


Figure 2 Unconstrained and constrained DSC melting endotherms for the original oriented PEN fibers.

range of the PEN fibers by using DSC experiments: the results of this are shown in Figure 2. The upper curve in the figure shows the melting endotherm of an unconstrained bundle of fibers and it is seen that the peak melting point is around 265°C. In most of the previous hot compaction studies, we have found that oriented polymers show a significant superheating effect, such that when under constraint they melt at a significantly elevated temperature compared to unconstrained melting. The lower melting endotherm in Figure 2, where the fibers were constrained by winding them around a crumpled DSC pan lid and tying in a knot, shows that this is also the case here for PEN fibers. The constrained peak melting temperature is seen to be just under 280°C, a shift upward of $\sim 15^\circ\text{C}$ compared to the unconstrained sample. As the fiber assembly is wound around a frame for the subsequent hot compaction trials, and also under a significant transverse pressure, the constrained melting behavior is more appropriate. Compaction tests were therefore carried out in the range of 268–276°C.

Figure 3 shows DSC melting endotherms for typical compacted samples made over this temperature range. As the compaction temperature was increased into the constrained melting range of the fiber, a second peak appeared with a peak melting temperature of 265°C, similar in position to the peak melting point of a completely melted sample as shown in the upper curve. We can therefore associate this peak with the production of the matrix phase: the higher the compaction temperature, the greater the percentage of the matrix phase produced up until the sample completely melts.

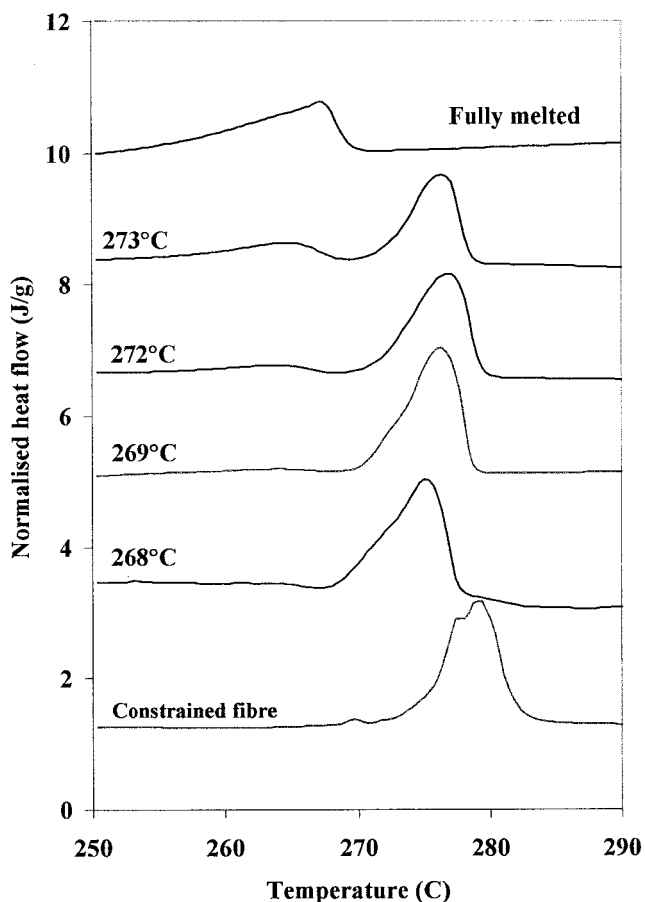


Figure 3 DSC melting endotherms of compacted bidirectional compacted samples.

Figure 4 shows the mechanical properties of samples made over this temperature range. The upper graph shows the dependence of the initial modulus with compaction temperature, whereas the lower graph shows the relationship of the in-plane strength to the compaction temperature. The results for both properties pass through a peak at around 271°C.

There are two opposing effects at work here, which lead to the maximum in these two parameters. As the compaction temperature is increased, the amount of the oriented phase falls as this is converted into the melted and recrystallized matrix phase, leading to a fall in the in-plane properties, which are dominated by the oriented component. The mechanical properties also depend on stress transfer between all the elements, and this improves as the amount of matrix increases. Therefore, the initial rise in properties at low compaction temperatures is due to the increase in coherency of the structure which is followed by a fall as the oriented component decreases significantly. The peak in the mechanical properties, or just after the peak, is one possible choice for the optimum compaction temperature, which here would be 271 or 272°C (corresponding to a matrix fraction of 10 to 15%). The

most common form for commercial usage of the compaction technology is in the form of a woven cloth, as described earlier. In this form, the weakness in the structure is the interlayer region between the woven layers, and previous research on other oriented polymers suggests that a matrix volume fraction of 20–30% is optimum to bond these layers together adequately. For such a percentage of melted material, 273°C would, therefore, be a more appropriate compaction temperature.

Dynamic mechanical tests

Figure 5 shows DMTA results for various PEN materials: the top graph shows the modulus versus test temperature, whereas the bottom graph shows $\tan \delta$. For the original fiber, the modulus at 30°C is around 22 GPa, falling monotonically to just under 5 GPa at a temperature of 200°C. If we take the peak in $\tan \delta$ as the position of the T_g , then this would be $\sim 160^\circ\text{C}$ for the original fiber (the average value for three tests was $160 \pm 5^\circ\text{C}$). To measure the matrix properties, a piece of completely melted material was used. For the matrix, the modulus at 30°C was found to be around 3 GPa, dropping to a very low value above its T_g , which was found to be $123 \pm 1^\circ\text{C}$ from three tests. The

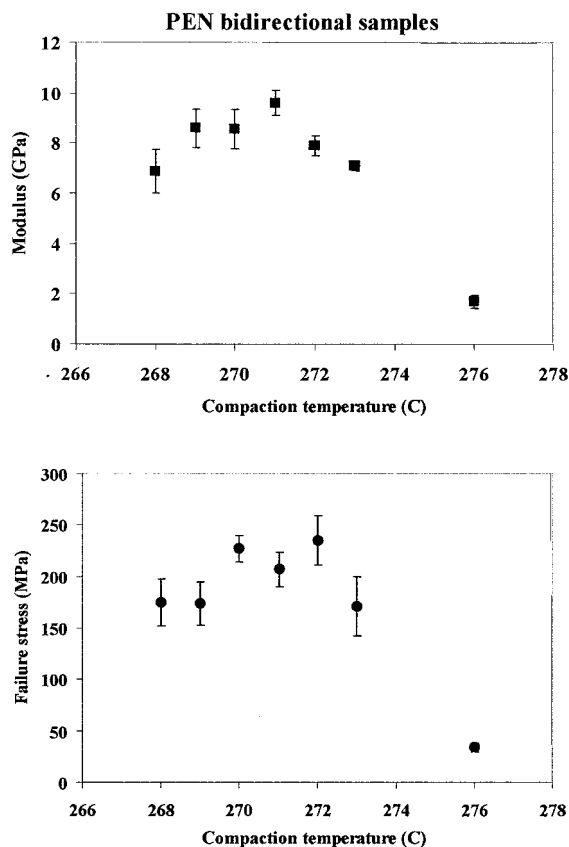


Figure 4 In-plane modulus and strength versus compaction temperatures.

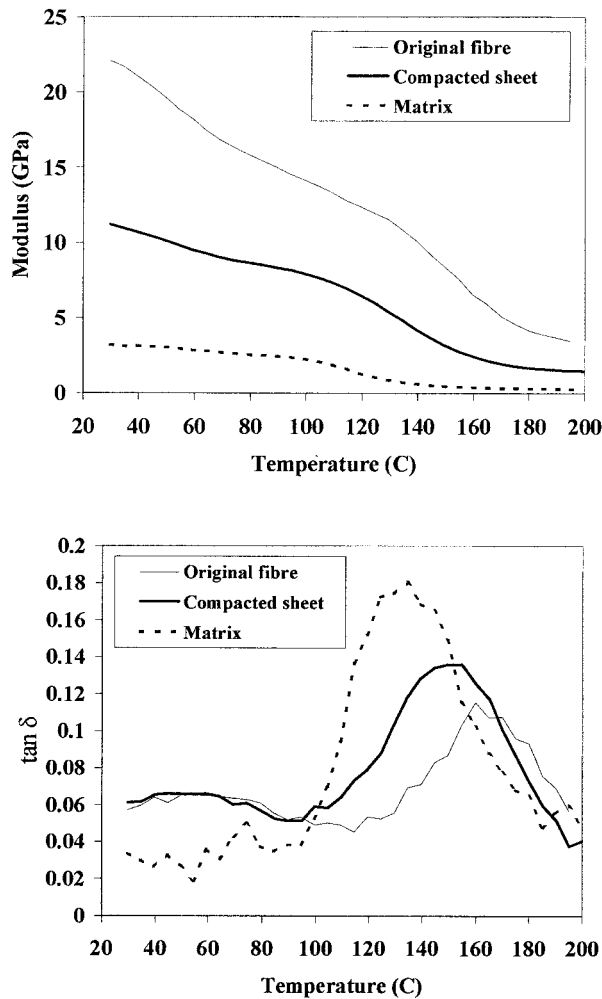


Figure 5 DMTA results for PEN materials.

compacted sheet used for these tests was that made at 271°C (12% matrix phase from DSC tests; Fig. 3). As would be expected, the properties of this material lay between the two component phases, with a modulus at 30°C of 12 GPa and a T_g of $149 \pm 4^\circ\text{C}$. It is likely that the lower position of the oriented peak in the compacted sheet (149°C compared to 160°C for the original fiber) is due to shrinkage and relaxation of molecular orientation as a result of the compaction process, as previously found with studies on PET.¹¹ As a result of this upper peak falling, and the low fraction of the matrix phase, the compacted sheet only showed a single combined broad relaxation peak, in contrast to the previous PET studies, which showed two distinct peaks due to a larger separation in the glass transitions of the fiber and matrix phases.

To corroborate this idea of the compacted PEN sheets as a composite whose properties depend on the properties of the two components (the oriented reinforcement and the melted and recrystallized matrix), we have previously used a modification of the simple rule of mixtures which assumes continuity of strain

between the components. For a unidirectional arrangement of the oriented phase, the Young's modulus of a compacted sheet $E_{\text{compacted}}$ would be given as

$$E_{\text{compacted}} = E_{\text{oriented}}V_{\text{O}} + E_{\text{melted}}V_{\text{M}} \quad (1)$$

where V_{O} and V_{M} are the respective volume fractions of the oriented and matrix phases and E_{oriented} and E_{matrix} are the respective Young's moduli. For a bidirectional sample, in any one direction, there will be a contribution from both the fibers that are aligned parallel and perpendicular to that direction so that the oriented component has to be split into a longitudinal component and a transverse component as

$$E_{\text{compacted}} = E_{\text{L}}\frac{V_{\text{O}}}{2} + E_{\text{T}}\frac{V_{\text{O}}}{2} + E_{\text{melted}}V_{\text{M}} \quad (2)$$

where E_{L} and E_{T} are the longitudinal and transverse modulus of the oriented fibers. If we make the assumption that the transverse modulus of the fiber E_{T} is the same as the isotropic modulus of the matrix, which is a good approximation for most oriented polymers, then we arrive at the final result:

$$E_{\text{compacted}} = \left(\frac{E_{\text{L}}}{2}\right)(V_{\text{O}}) + E_{\text{M}}\frac{(1 + V_{\text{M}})}{2} \quad (3)$$

By using the values from Figure 5, and the fraction of the two phases previously measured from DSC ($V_{\text{M}} = 12\%$, $V_{\text{O}} = 88\%$ for the sample manufactured at 271°C), we can predict the compacted sheet modulus over the measured temperature range, which is shown in Figure 6. The graph shows that the agreement between the measured compacted sheet modulus and that predicted by the simple rule of mixtures based on

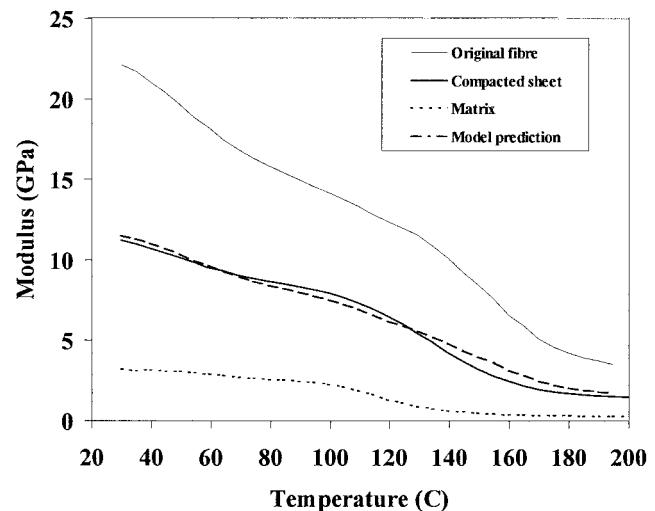


Figure 6 A comparison of the measured and predicted temperature performance of the compacted sheet modulus.

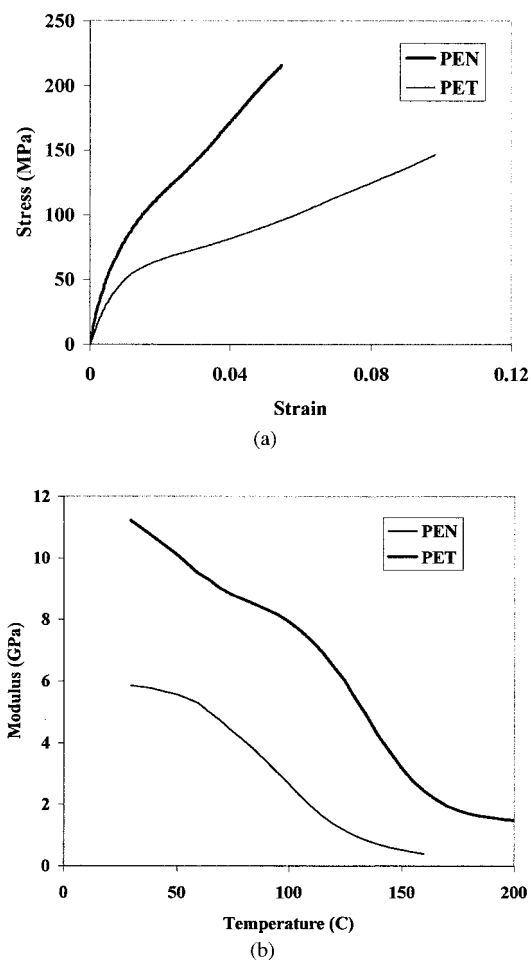


Figure 7 (A) Tensile stress–strain curves for optimum samples of PEN and PET. (B) DMTA temperature scans for optimum samples of PEN and PET.

the properties of the two phases is excellent over the whole temperature range. The transition of the model prediction is smoother than seen in the actual material, due most likely to the fall in the T_g of the oriented phase associated with the compaction process, as described above. These results confirm that compacted PEN can be understood as a composite with continuity of strain between the phases, at least for the Young's modulus.

Comparison with pet

A key aspect of this study was to compare the properties of compacted PEN with those of compacted PET sheet determined in a previous study.¹¹ Figure 7 shows a comparison of the tensile stress–strain behavior, and DMTA temperature performance, of optimum compacted PEN and PET samples: the key mechanical results are also tabulated in Table II.

Compacted PEN sheet is seen to have improved mechanical properties over compacted PET, with a significantly greater tensile modulus and a higher T_g . For the DMTA results, we see that the modulus at 120°C for PEN is still greater than that of PET at room temperature (+20°C). The strain to failure for PEN is lower than PET, as would be expected from the respective properties of the oriented fibers, and future work will explore whether this leads to a reduction in impact strength and thermoformability when compared to PET.

The issue of whether PEN has an advantage over PET in terms of improved hydrolytic stability has yet to be properly addressed. Samples made by using a longer dwell time at the compaction temperature (10 min rather than the 2 min used throughout this work as determined from the previous PET work) did show significant embrittlement, suggesting that significant hydrolytic degradation can occur in PEN. Future work will address this important issue in greater detail.

CONCLUSION

The results obtained for compacted PEN fibers are very encouraging, showing a high tensile modulus (~ 10 GPa for a bidirectional sheet) and a T_g of $\sim 150^\circ\text{C}$: both values are a significant improvement on the values for compacted PET of ~ 6 GPa and 110°C , respectively. The bidirectional arrangement of fibers, used in these experiments, allowed a homogeneous sheet to be produced with a relatively low percentage of the melted and recrystallized matrix ($\sim 12\%$), giving excellent retention of the oriented fiber properties in the compacted composite. It was shown that the Young's modulus of the compacted sheet could be predicted to a good approximation based on the prop-

TABLE II
A Comparison of the Properties of the Optimum Compacted Samples of PEN and PET

	Compaction temperature (°C)	Tensile modulus (GPa)	Tensile strength (MPa)	Tensile failure strain (%)	Modulus at +120°C (DMTA) (GPa)	T_g (°C)
PEN	271	9.6 ± 0.5	207 ± 17	5 ± 0.4	6.53	149 ± 4
PET	257	5.8 ± 0.2	130 ± 11	11 ± 1	1.58	110 ± 1

erties of the oriented and matrix phases, the proportion of each phase, and a simple rule of mixtures.

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