

Hot Compaction of Woven Nylon 6,6 Multifilaments

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ABSTRACT: We describe a study of the hot compaction of woven nylon 6,6 multifilaments produced by a patented procedure, developed at the University of Leeds, for creating novel single-polymer composites. In this process, an assembly of oriented elements, often in the form of a woven cloth, is held under pressure and taken to a critical temperature so that a small fraction of the surface of each oriented element is melted, which on cooling recrystallizes to form the matrix of the single-polymer composite. This process is therefore a way of producing novel high-volume-fraction polymer/polymer composites in which the two phases are chemically the same material. Nylon is an obvious candidate material for this process because oriented nylon multifilaments are available on a commercial scale. The aim of this study was first to establish the conditions of temperature and pressure for the successful hot compaction of oriented nylon 6,6 fibers and second to assess the mechanical properties of the manufactured hot-compacted nylon sheets. A crucial aspect of this work, not previously examined in hot-compaction studies of other oriented polymers, was the

sensitivity of the properties to absorbed water, with a significant change in the properties measured immediately after hot-compaction processing and 2 weeks later when 2% water had been absorbed by the compacted nylon sheets. As expected, the water uptake had a greater effect on those properties that depended on local chain interactions (e.g., the modulus and yield strength) and less effect on those properties that depended on the large-scale properties of the molecular network (e.g., strength). The only negative aspect of the properties of the hot-compacted nylon sheets was the elevated-temperature performance of the wet sample, with the modulus falling to a very low value at a temperature of 80°C. However, apart from the elevated-temperature performance, the majority of the measured properties of the hot-compacted nylon sheets were comparable to those of hot-compacted polypropylene and poly(ethylene terephthalate). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 991–997, 2006

Key words: nylon; self-reinforced polymer composites; mechanical properties

INTRODUCTION

Research carried out at Leeds University over the last 10 years has shown that the hot-compaction process can be widely applied to oriented polymers for the production of novel polymer/polymer composites. The concept of single-polymer composites was first described by Capiati and Porter¹ using oriented polyethylene filaments and polyethylene powder with different melting points. Other techniques reported in the literature include film stacking, powder impregnation, and solvent impregnation,^{2–6} bicomponent tapes with an outer, lower melting point layer,⁷ and pressure-controlled melting.⁸ In the procedure developed at Leeds,⁹ the distinction from the majority of these other studies is that only a single component is used. Assemblies of oriented fibers or tapes (often in the form of woven cloth) are taken to a critical temperature, while under a small constraining pressure. At the critical temperature, a thin skin on the surface of each oriented element melts, and on cooling, this recrystallizes to form the matrix of a single-polymer composite,

with the remaining oriented fraction acting as the reinforcing phase. The virtue of this technique is that the matrix phase is produced around each fiber, negating the need for infiltration, and that molecular continuity is achieved between the two components of the final composite.

The original research work was carried out on melt-spun polyethylene fibers^{10,11} and used a mixture of mechanical tests and detailed morphological analysis to elucidate the compaction mechanisms. Subsequent research has shown that a similar process, albeit with a different critical temperature for each material, can be applied to a wide range of oriented semicrystalline polymers, including gel-spun polyethylenes,^{12–14} polypropylene (PP),^{15–18} poly(ethylene terephthalate) (PET),^{19,20} and poly(ethylene naphthalate):²¹ a review of these studies can be found in ref. 22.

Oriented nylon fibers are another obvious candidate for investigation, and we have taken advantage of the availability of a commercially produced woven nylon cloth made from high-tenacity nylon 6,6 multifilaments. Differential scanning calorimetry (DSC) was used to determine the temperature range for the initial compaction trials: a compaction temperature of 261°C was found to be optimum. As with all nylons, the uptake of water moisture is a key issue, and so exper-

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iments were carried out immediately after compaction (when the sample was effectively dry) and after conditioning at 50% relative humidity (RH): the equilibrium water uptake was found to be 2.2 wt % after 2 weeks. Stress-strain tests were undertaken to assess the effect of the water uptake on the mechanical properties, and dynamic mechanical analysis (DMTA) measurements were used to compare the effect of the water uptake on the upper usage temperature. As with the previous studies, a key aspect to understanding the properties of the hot-compacted sheets was to understand the properties of the two components of the composite, namely, the reinforcing elements and the melted and recrystallized matrix phase. When possible, experiments were carried out on these two materials, both in the dry state and at the equilibrium water content for 50% RH.

EXPERIMENTAL

Materials

The woven nylon 6,6 cloth (plain weave) was supplied by BP Amoco Fabrics GmbH (Gronau, Germany). The warp and weft yarns were made from identical high-tenacity yarn with a strength of 235 dtex (~ 800 MPa). The density of the nylon filaments was measured to be 1140 kg/m^3 with a gravimetric method.

The molecular weight of the original nylon filaments was measured with the intrinsic viscosity (η) method. An Ubbelohde dilution viscometer was suspended in a water bath at 25°C , and 0.125 mg of each sample was dissolved in 25 mg of the chosen solvent of formic acid (90%). Measurements were then 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 η to be determined by extrapolation to a zero concentration. The number-average molecular weight (M_n) could then be obtained from the Mark-Houwink relationship:

$$\eta = kM_n^\alpha \quad (1)$$

where k and α are the Mark-Houwink parameters. Burke and Orefino²³ used a variety of experimental techniques to determine the values of these two parameters for nylon 66 in a 90% solution of formic acid: k was determined to be 3.53×10^{-4} , and α was determined to be 0.786 at 25°C . These measurements gave an M_n value of $32,552 \text{ g/mol}$.

Sample manufacture

In the most recent hot-compaction studies (e.g., the work on PET²⁴), we developed a procedure by which the layers of woven cloth to be compacted are placed between brass plates, rather than using a matched

metal mold. This enables rapid heating and cooling and restricts the time that the oriented fibers have to spend at the elevated temperature. This procedure is also the closest approximation of the commercial process used to make hot-compacted PP sheets. Silicon rubber sheets are placed between the brass sheets and the layers of woven cloth to produce even pressure over the assembly.

The compaction procedure was as follows. First, the cloth layers were placed in a vacuum oven overnight (16 h) at 80°C to remove any absorbed water. Second, eight layers of woven nylon 66 cloth (125 mm^2) were assembled between the rubber sheets, followed by outer layers of polytetrafluoroethylene release film and soft aluminum to aid in the release after compaction and finally the brass sheets. A thermocouple was placed between the central two layers of the cloth to monitor the temperature of the assembly during the compaction procedure.

For compaction, the hot press was first set to the appropriate compaction temperature and allowed to equilibrate. The assembly was then placed in the hot press, a small compaction 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 dwell time of 2 min , after which it was cooled rapidly with water circulated around the hot press platens.

Mechanical testing

The in-plane modulus and strength of the compacted samples were measured according to the guidelines of ASTM D 638. The tests were carried out with an RDP Howden servomechanical test machine (Southam, UK), and the sample strain was measured with a Messphysik video extensometer (Southam, UK). The tests were carried out at a nominal strain rate of $2 \times 10^{-3} \text{ s}^{-1}$. An important issue was the effect of water absorption on the mechanical properties. For this reason, tests were carried out either immediately after compaction (15 min) or after conditioning at 50% RH until an equilibrium water content was achieved. The conditioning of the samples was carried out by their placement in a jar containing a saturated calcium nitrate solution. Tests were also carried out on the original nylon filaments and on samples taken from sheets made by completed melting layers of the woven nylon fibers. These melted samples were made to represent the matrix of the hot-compacted samples. Both the fibers and matrix were tested at various water contents.

The bonding that developed during compaction was measured with a T-peel test (after ASTM D 1876). Samples for this test were made by the placement of a 10-mm -wide strip of thin aluminum foil between the

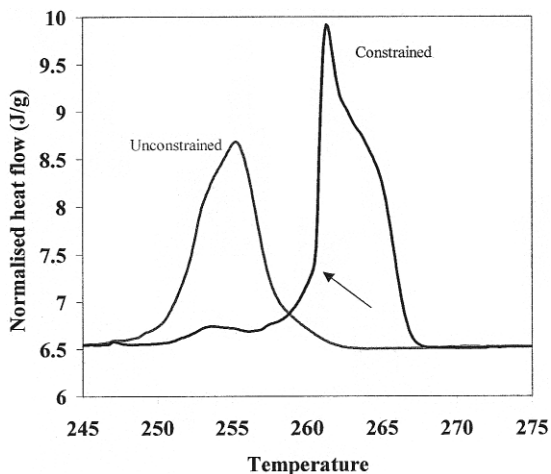


Figure 1 DSC melting endotherms for the original nylon 6,6 fibers.

central two layers of cloth in the compaction assembly. The width of the peel samples was 10 mm, so the results are presented as the peel load/10 mm. The peel tests were carried out at a displacement rate of 80 mm/min.

DSC

The melting behavior of the original fibers and compacted sheets was determined with a PerkinElmer DSC-7 (Beaccusfield, UK) at a scanning rate of 10°C/min.

DMTA

The performance of the compacted nylon samples at elevated temperature was determined by dynamic mechanical thermal analysis. The measurements were carried out in bending with a Rheometrics RSAII solids analyzer (Alzenau, Germany) with a sinusoidal strain of ±0.05% at a frequency of 1 Hz.

RESULTS

Determination of the optimum compaction temperature

To determine the appropriate temperature range for the preliminary compaction experiments, the melting behavior of the original nylon filaments was investigated with DSC. An important issue is to assess the melting behavior of the oriented elements when constrained because, as described in the Experimental section, a pressure of 2.8 MPa is applied to the woven-fiber assembly during compaction to restrain the fibers from shrinking and the associated loss of molecular orientation that would follow. Figure 1 shows melting endotherms of nylon 6,6 filaments taken from the

woven cloth, tested both unconstrained and constrained. For the constrained test, the fiber was wound around a crumpled aluminum pan lid and then tied in a knot.¹² The figure shows a significant increase in the onset of melting due to constraint of around 10°C. At first sight, the melting peak for the constrained fiber may appear to be an unusual shape. However, once the constrained fiber begins to melt (at a temperature indicated by the arrow), it breaks, the constraint is released, and the fiber melts very quickly because its temperature is 10°C above its melting point: this is associated with a significant increase in the slope of the melting endotherm. In the hot-compaction process, the constraint is applied by an external pressure and therefore remains constant as the fiber begins to melt.

These DSC results suggest a starting temperature of 260°C for the compaction experiments, so samples were made at 260, 261, 262, 263, and 264°C. DSC tests were carried out on these samples, and representative results are shown in Figure 2. The fully melted sample was that made at 264°C, and this suggests that this compaction temperature was too high. It is useful to have this DSC analysis of a completely melted sample, as this indicates the temperature at which we would expect to see a peak in the compacted samples associated with the melted and recrystallized matrix phase, seen here to be around 261°C. This is close to the peak melting temperature for the original fiber, around 265°C, making it difficult to ascertain the two phases unless there is a significant loss of the oriented phase, as seen in the sample made at 263°C. The sample made at 261°C appears close to the optimum, and this was the temperature used for the remainder of the compaction experiments.

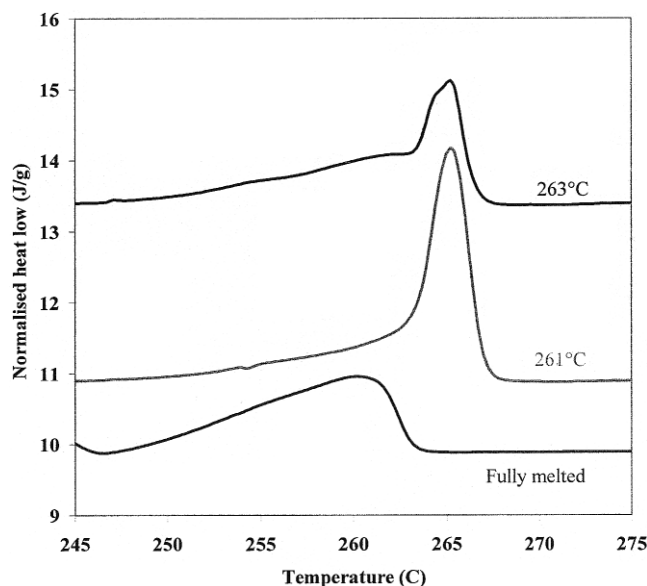


Figure 2 DSC melting endotherms for compacted samples.

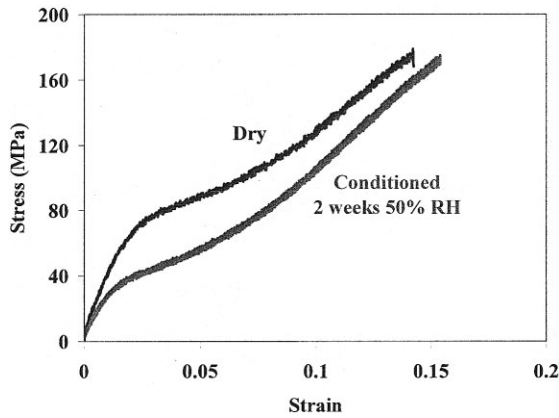


Figure 3 Stress-strain curves for optimum compacted samples (261°C) tested dry and after 2 weeks at 50% RH (~2% absorbed water).

Effect of absorbed water on the compacted-sheet properties

It is well known that nylon absorbs a significant amount of water because of the hydrogen bonding in the polymer. A compacted nylon sheet is therefore likely to show significantly different properties directly after it has been compacted (the fiber having been dried beforehand) and after it has been equilibrated at room humidity. To establish the uptake of water, a piece of a compacted sample was weighed directly after compaction and then placed in a chamber containing a saturated calcium nitrate solution (50% RH). The sample was removed from the chamber at various times and weighed to determine the water uptake. The water uptake was found, as expected, to be Fickian (i.e., the uptake percentage was proportional to the square root of time), and after 2 weeks, it had stabilized at a level of 2.2 wt %.

To compare the effect of the water uptake on the properties, compacted samples were conditioned for 2 weeks in the same chamber. Figure 3 shows a comparison of typical stress-strain curves for a dry sample (tested 15 min after compaction) and a wet sample (2.2% absorbed water). Table I shows typical values for the initial Young's modulus, yield point, and failure stress for the two samples. As might have been expected, the initial modulus and yield stress are affected by the absorbed water (being sensitive to local chain separation),

TABLE I
Effect of the Compacted Sheet Properties on the Water Content

	Initial modulus (GPa)	Yield stress (MPa)	Ultimate strength (MPa)
Dry	4.1	75	170
2.2% absorbed water	2.8	35	170

whereas the ultimate strength is little affected, being sensitive to a larger scale network property. For information, the results shown here are for testing parallel to the warp direction of the original cloth. The ultimate strength in the weft direction was lower and was measured to be 130 MPa for both the dry and wet samples.

As a complementary study, tests were also carried out to assess the effect of water on the matrix phase on the compacted nylon composites. Sheets of completely melted material were made via processing at 270°C with a dwell time similar to that used for the compacted sheets and with the same cooling procedure. Water uptake tests, carried out as described previously for the compacted samples (after first drying overnight at 80°C), showed the equilibrium water content to be higher than that found for the compacted sheets, with a value of 2.7 wt %. From this, we can suggest that the oriented fibers absorb less water to account for the difference. Using a simple rule of mixtures and a knowledge of the fractions of the oriented and matrix components (V_{oriented} and V_{matrix} , respectively) in the compacted sheet, we can estimate the water percentage in the oriented fibers ($\text{Oriented}_{\text{water}\%}$) as follows:

$$\text{Comp}_{\text{water}\%} = \text{Oriented}_{\text{water}\%} V_{\text{oriented}} + \text{Matrix}_{\text{water}\%} V_{\text{matrix}} \quad (2)$$

where $\text{Comp}_{\text{water}\%}$ and $\text{Matrix}_{\text{water}\%}$ are the percentages of water in the compacted sheet and matrix, respectively. Normally, we can determine V_{oriented} and V_{matrix} from DSC measurements similar to those shown in Figure 2. However, with the peak melting points of the two components being close together and difficult to resolve, this is not possible. In all the previous studies, an optimum compacted woven sheet was usually found to have a matrix volume fraction of

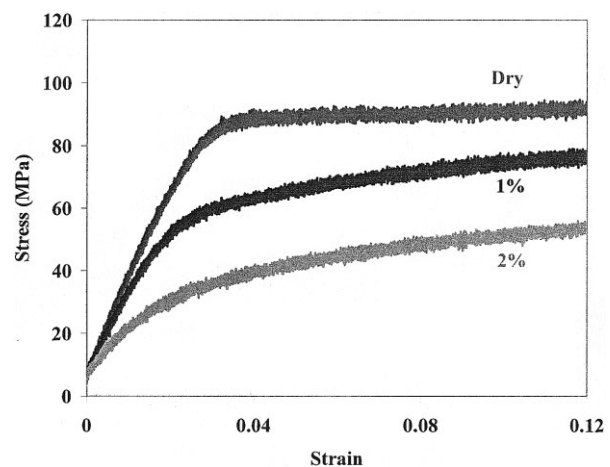


Figure 4 Stress-strain curves for completely melted samples (matrix) tested dry and with 1 or 2% absorbed water.

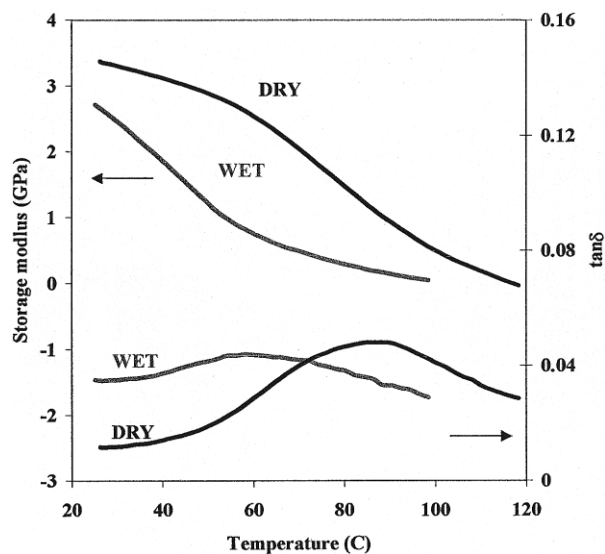


Figure 5 DMTA temperature scans of a dry optimum compacted sample and a wet sample conditioned at 50% RH ($\sim 2.2\%$ absorbed water).

30%. Using this value would predict that the oriented nylon fiber contains 2 wt % absorbed water.

Figure 4 shows stress-strain curves of nylon matrix samples tested dry and with 1 or 2% absorbed water. When the nylon 6,6 is dry, it is linear up to a sharp yield point at a stress of around 90 MPa. As the water content increases, the initial Young's modulus and yield stress fall significantly. Typical values of the modulus were 3.1 GPa for the dry sample and 1.91 GPa for the sample equilibrated at 50% RH (2.7% w/w water uptake). With 2% absorbed water, the behavior is more nonlinear, and this made it difficult to pick out a clear yield point. It is clear that these changes in the matrix behavior will have a significant effect on the properties of the compacted sheet tested dry and wet, as shown earlier in Figure 3, which also shows a reduction in the modulus and yield point with increased water absorption.

It is very likely that the oriented fiber properties also change with the water uptake. This proved difficult to

measure for two reasons: first, the fibers had a large amount of crimp, which made a measurement of the initial modulus uncertain, and second, it was not possible to dry the fibers without shrinkage occurring, which was associated with a loss of orientation and properties.

Another important test for a compacted sheet is the peel strength. This test probes a potential weak point of the structure, which is the thin layer of matrix material between each woven layer. To test this, samples are manufactured with a 10-mm-wide, thin layer of aluminum foil between the central two cloth layers and located at one side of the sample. After compaction, this acts as a starter crack located at the intralaminar boundary: a T-peel test is then carried out, and the average peel load is measured for a 10-mm-wide strip. Typical peel load values measured were 23 ± 3.2 N/10 mm for the 50% RH conditioned sample (2.2% absorbed water) and 17.2 ± 2.1 N/10 mm for a dry sample. Both of these values are among the highest measured for any compacted material and are compared to other materials in the next section.

The final test carried out was a DMTA temperature scan. Here a very small sinusoidal strain ($\pm 0.1\%$) is applied to the sample while the temperature is ramped at $2^\circ\text{C}/\text{min}$ from 25°C up to an elevated temperature. At each chosen temperature, a measurement is made of the storage modulus (E'), the loss modulus (E''), and the loss factor ($\tan \delta = E''/E'$). Figure 5 shows the variation of E' and $\tan \delta$ with temperature for a 50% RH conditioned sample (2.2% absorbed water) and a dry sample. In addition to a lower modulus at room temperature as measured from the stress-strain measurements, the modulus of the sample with 2.2% absorbed water falls much more rapidly with increasing temperature in comparison with the dry sample. The glass-transition temperature, taken here as the temperature at which $\tan \delta$ is a peak, increases from 58°C for the sample with 2.2% absorbed water to 90°C for the dry sample.

Comparison with other compacted sheets

In the final section of this article, we compare the properties of hot-compacted dry and wet nylon 6,6

TABLE II
Comparative Properties of the Compacted Sheets

	Dry nylon	Wet nylon (2.2% water)	PP	PET
Compaction temperature ($^\circ\text{C}$)	261	261	191	258
Oriented-phase modulus (GPa)		5.8	10.8	14
Matrix-phase modulus (GPa)	3.1	1.9	1.2	2.8
Compacted-sheet density (kg/m^3)	1140	1140	910	1400
Compacted-sheet initial modulus (GPa)	4.1	2.8	5.06	5.82
Compacted-sheet strength (MPa)	150 ^a	150 ^a	182	130
Compacted-sheet peel strength (N/10 mm)	17 ± 2	23 ± 3	8 ± 1	18 ± 4

^a Average of warp and weft values.

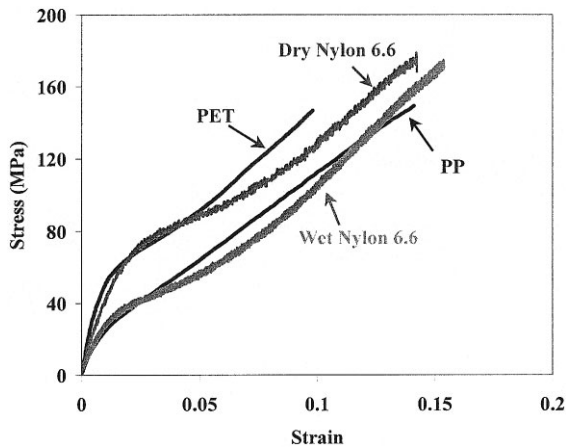


Figure 6 Stress-strain curves for optimum compacted samples at 20°C.

with those of PP and PET determined from previous studies: a comparison of various properties of these four hot-compact materials is shown in Table II.

Figure 6 compares typical stress-strain curves for these four materials. Dry nylon 6,6 is similar in terms of modulus and yield stress to PET, whereas wet nylon 6,6 is similar to PP. The ultimate strength of the compacted nylon sheets, which is independent of the amount of absorbed water, is similar for all four materials.

Figure 7 compares the stress-strain curves of the four matrix materials from measurements on the associated melted sheets. Dry nylon has the highest yield strength because of the hydrogen bonding present, followed by PET, wet nylon, and PP (in that order). This ranking of the matrix materials has a direct result for the intralaminar strength of the hot-compact materials, as measured by the peel test. Peel test average values of 23 ± 3 , 18 ± 4 , 17 ± 2 , and 8 ± 1 for wet nylon 6,6, PET, dry nylon 6,6, and PP,

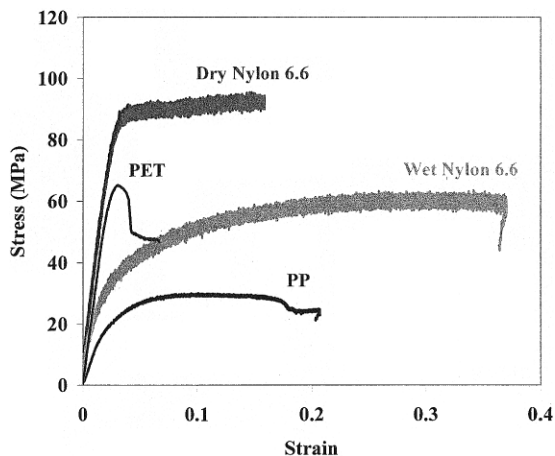


Figure 7 Comparison of the stress-strain curves of matrix phases for various hot-compact sheets.

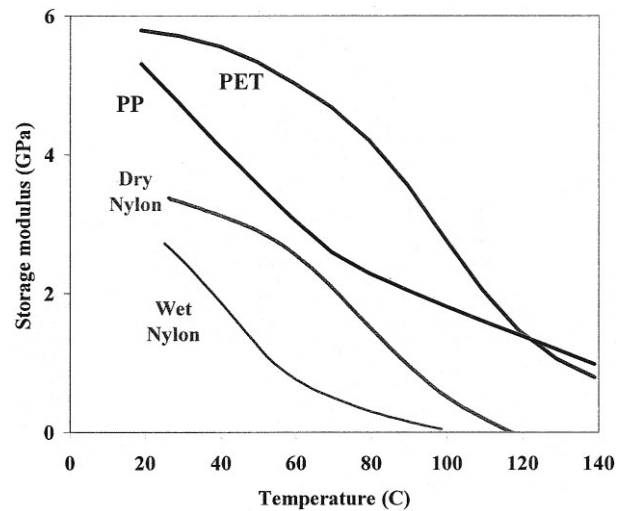


Figure 8 DMTA temperature scans for various hot-compact sheets.

respectively, are directly proportional to the yield stress of the pure polymer; this suggests a direct link between the cohesive strength of the polymer and the peel strength of the single-polymer composite.

Figure 8 compares DMTA scans for the four hot-compact materials. To some extent, the temperature performance scales with the room-temperature modulus, so the higher this is, the better the performance is at elevated temperatures. The properties of the wet nylon sample do fall quite rapidly as the temperature is increased.

As a final comment on the relative performance of the hot-compact sheets, the density of the nylon 6,6 sheets, at 1140 kg/m^3 , is larger than that of PP (910 kg/m^3) but lower than that of PET (1400 kg/m^3).

CONCLUSIONS

In this article, we have described how hot-compact sheets can be manufactured from layers of woven high-tenacity nylon 6,6 multifilaments. As with all nylon-based materials, the properties are sensitive to the amount of absorbed water. The properties of compacted nylon 6,6 are good at room temperature, with the stress-strain behavior in the dry state being similar to that of compacted PET sheets, whereas in the equilibrated state (2.2% absorbed water), the stress-strain behavior is similar to that of PP. In terms of the intralaminar peel strength, the high cohesive strength of nylon results in an excellent value for this property, better than that of either PP or PET. In terms of higher temperature exposure, the compacted nylon sheets show poorer performance than PP and PET, particularly the sample with 2.2% absorbed water. However, if elevated-temperature performance is not an issue,

then compacted nylon sheets have properties comparable to those of compacted PP and PET.

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