DEVELOPING THE NEXT GENERATION OF SELF-REINFORCED POLYMER COMPOSITES

I.M. Ward, A.P. Unwin, P.J. Hine and M.J. Bonner

School of Physics and Astronomy, IRC in Polymer Science and Technology, University of Leeds, U.K.

KEYWORDS: Self-reinforced polymer composites: hot compaction: mechanical properties.

ABSTRACT

This paper presents developments in the field of hot-compaction of oriented polymers to produce self-reinforced single polymer composites. Currently, the commercial applications of hot compacted products are based on polypropylene and we have been investigating the feasibility of extending the process to other polymers such as polyethylene (PE), poly (ethylene terephthalate) (PET) and nylon. Of these materials, PE and PET offer considerable potential although there are significant obstacles to be overcome before commercial exploitation can proceed. This paper discusses how these problems are being tackled.

1. INTRODUCTION

Self-reinforced single polymer composites have now emerged as a new theme in the area of polymer composites. Several groups have addressed this area with a range of techniques, including film stacking, powder impregnation and co-extrusion of films. We have tackled this at Leeds through a patented hot compaction process [1]. In this process, an assembly of oriented polymer fibres or tapes is subjected to a combination of pressure and temperature, that causes selective melting of the surface layers of the oriented elements, and then cooled so that this melted material can recrystallise to form the matrix phase bonding together the remaining bulk of the oriented elements. Research and development work was undertaken in a spin-off company, Vantage Polymers Ltd., set up under the auspices of Leeds University. This led to the establishment of a continuous process for the commercial production of hot-compacted sheets, based on woven oriented polypropylene tapes, and the identification of potential commercial applications. Since 2000 the commercial developments have been undertaken by Propex Fabrics GmbH, Gronau, Germany (initially B.P.) who manufacture Curv® self-reinforced polypropylene. A wide variety of products have been established including sports protection (Nike shin pads), luggage (Samsonite X-lite suitcases) and loudspeakers (Wilson Benesch). Other applications include automotive panelling and anti-ballistics.

Research at Leeds University has shown that the hot compaction technique can be applied to many polymers other than polypropylene [2, 3]. In the case of polyethylene there has been much research on both melt-spun and gel-spun fibres, mostly in collaboration with Professor Bassett and Robert Olley at Reading University. Preliminary studies have also been undertaken at Leeds on poly(ethylene terephthalate), poly(ethylene naphthalate), nylon and liquid crystalline polymers. Recently, we have embarked on a programme of work [4] exploring the commercial viability of other polymers, including polyethylene (PE), poly (ethylene terephthalate) (PET) and nylon, and aimed specifically at tackling such problems as high processing temperatures, the width of the processing window and the thermoformability of the hot-compacted product. This paper describes the progress achieved in the case of polyethylene, poly (ethylene terephthalate) and nylon.

2. EXPERIMENTAL

2.1 Sample preparation

A fundamental goal of the hot compaction process is to transfer the beneficial mechanical properties of an oriented tape or fibre to a two dimensional sheet and this is generally achieved by the heat treatment under pressure of a suitable arrangement of the oriented phase. The simplest way to control the arrangement of the oriented phase is through a prior weaving stage and this is generally the approach we use. In the samples discussed here, the oriented phase can be fibre or tape, the arrangement is usually woven but can be of different weave style and interleaved film may or may not be used. Figure 1 shows an example of three woven layers of a tape with two interspersed layers of film and the resulting hot-compacted product would be referred to as 3-ply with interleaved film.

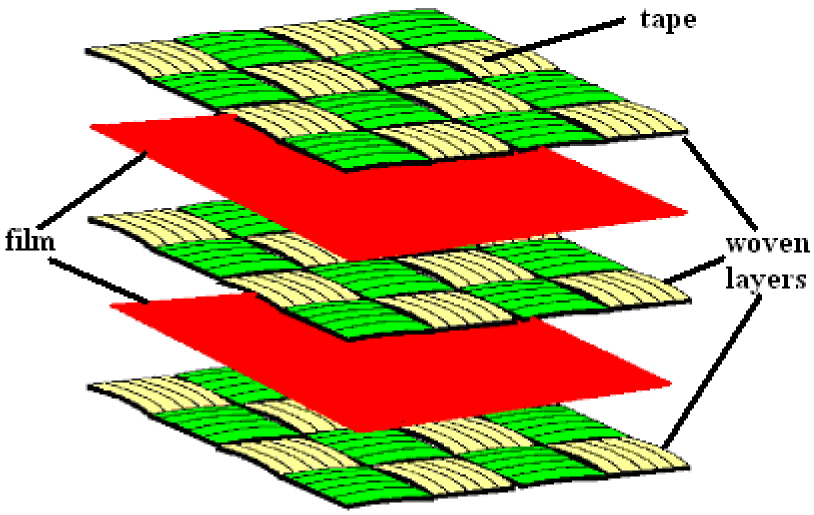

Figure 1: A typical arrangement used in the production of hot compacted polymer sheets

Compacted samples were prepared by pressing stacked arrangements, similar to that shown in Figure 1, between the heated platens of a hydraulically operated press at a range of temperatures and using a pressure of about 700psi. A thermocouple, inserted between the middle two layers of material, allows the local temperature to be monitored. A typical compaction cycle is shown in Figure 2. The heating stage, which can take 5 to 6 minutes, is the time taken to get to within 0.5°C of the target annealing temperature. The dwell time is the time interval over which the sample temperature is maintained within 0.5°C of the annealing temperature and is one of the variables used in exploring the hot-compaction process. At the end of the dwell time a rapid cooling stage is initiated by passing cold water through the platens. For the example shown in Figure 2 the annealing time is quoted as 2 minutes.

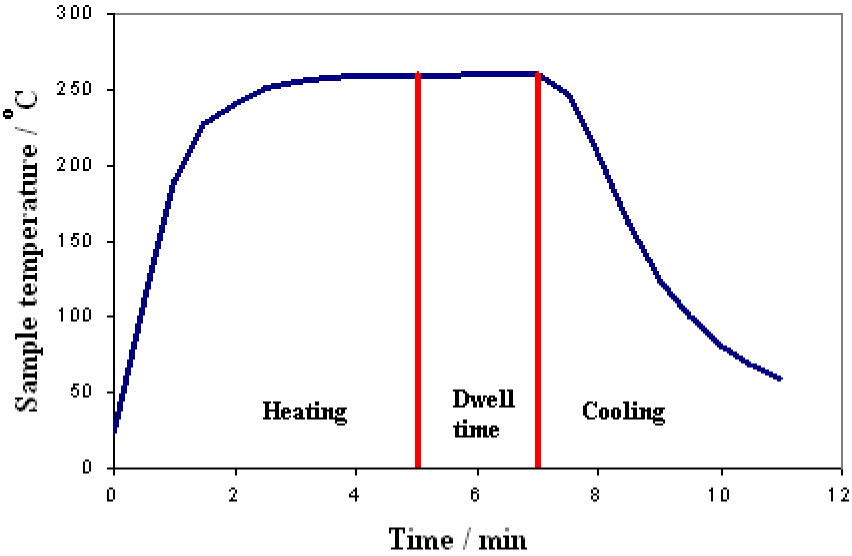

Figure 2: A typical hot-compaction cycle

The typical dimensions of sheets produced using arrangements such as that shown in Figure 1 and using a compaction cycle similar to that shown in Figure 2 is about 120 mm square. The polymers investigated were PP, PE, nylon and PET. Strips, parallel to one of the principal directions (warp or weft in the woven cloth), were cut from these sheets and subjected to a range of mechanical tests. Factors that have been investigated include variations in weave style and the incorporation of thin film between the woven assemblies prior to hot compaction.

2.2 Mechanical measurements

The effectiveness of the hot compaction process has been assessed by a range of mechanical tests, including measurements of peel strength, stress strain analysis in uniaxial tension and dynamic mechanical analysis. Peel tests were performed at room temperature using an RDP tensile testing machine on strips of material, typically 1 cm in width, cut from the compacted sheets. The test involves measuring the force required to separate the central two layers of the compacted sheet using a constant crosshead speed of 80 mm min^{-1}. Small strain tensile tests were performed on the same machine using a grip separation of 60 mm and a crosshead speed of 2.5 mm min^{-1}, corresponding to an initial strain rate of approximately 10^{-3} s^{-1}. The local strain on the sample was obtained by using a videoextensometer to follow the relative displacement of two targets, drawn in tippex on the surface of the sample. Large strain tensile experiments were performed at a higher strain rate, typically 10^{-2} s^{-1}. Dynamic mechanical tests were performed over a range of temperatures in dual cantilever mode at a frequency of 1 Hz and using a central displacement corresponding to a peak strain of about 0.2%.

In the following sub-sections we present some key results obtained from these tests on specific materials to help illustrate certain advantages and disadvantages before embarking on a more general assessment of future prospects for these materials.

2.2.1 Peel strength

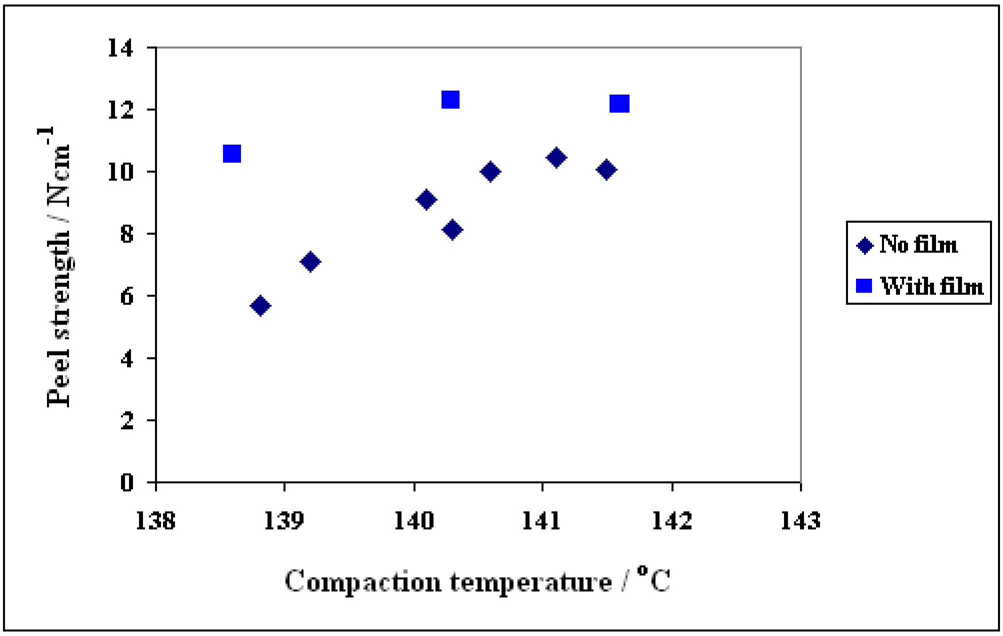

Figure 3: Typical peel test results for hot-compacted Certran polyethylene fibre.

Figure 3 illustrates how the peel strength varies with the compaction temperature for two sets of hot-compacted polyethylene sheets. For all samples the oriented phase is a fibre form of highly oriented polyethylene, Certran. The woven cloth is a unidirectional weave on a PET carrier but individual layers have been arranged so that there is a balanced orientation in the compacted sheet. All samples are constructed from 4 layers of cloth (4-ply) using a dwell time of 5 minutes and a compaction pressure of 700psi. The difference between the two sets is that one uses three layers of interleaved polyethylene film. Considering the samples without interleaved film first, it is clear that the peel strength increases with compaction temperature with values of about 10Ncm^{-1} shown by samples compacted at 141°C. The use of interleaved film allows us to achieve a slightly higher peel strength. Both these observations, an increase in peel strength through increased compaction temperature or through the use of interleaved film, are common in most polymers amenable to the hot-compaction process. An important observation from Figure 3 is that the improvement in peel strength achieved through incorporation of the interleaved film is more significant at the lower compaction temperatures. The net effect of this is to widen the processing window for this material and this feature provides polyethylene with a significant advantage.

2.2.2 Stress strain curves and modulus

Figure 4 shows results of the 0.1% Young's modulus for the samples considered in Figure 3. The trend for the modulus to decrease as the compaction temperature is increased is typical and is attributed to the melting and recrystallisation in a non-oriented disposition of larger proportions of the original oriented phase. For a balanced sheet (fibre phase oriented in two principal directions) the modulus is typically about or less than half that of the original oriented phase, depending on the proportion of fibre phase remaining in the hot-compacted sheet. The introduction of interleaved film will typically result in a reduction of the modulus, because of the greater proportion of nonfibre phase but the magnitude of the change depends on the thickness of the film used. In this case, the interleaved film does not have a significantly detrimental effect on the modulus. This, coupled with the effect of interleaved film on the peel strength, reinforces the observation of a widening of the processing window in polyethylene when interleaved film is used.

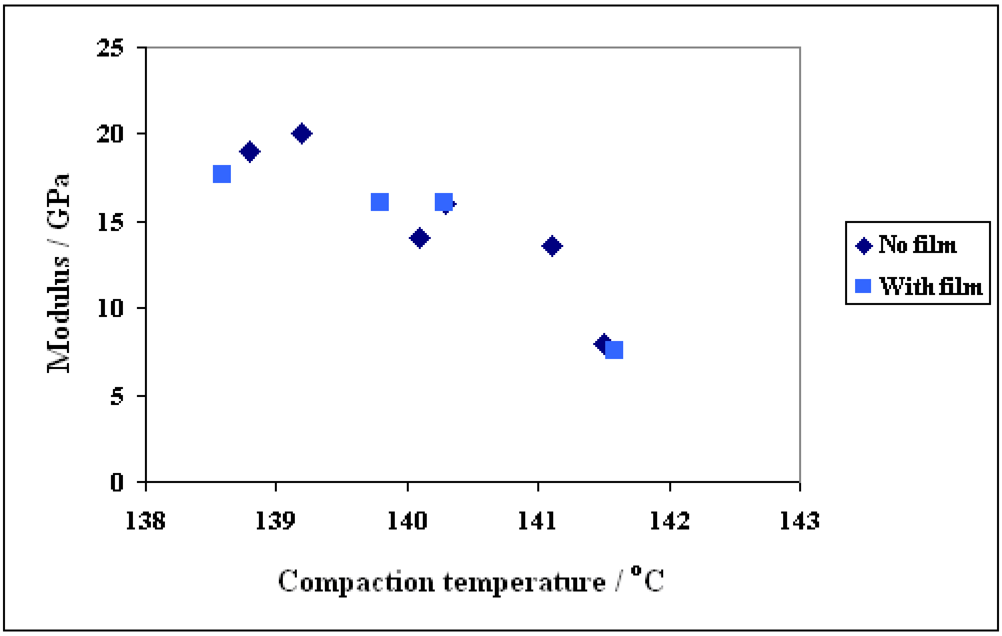

Figure 4: Typical modulus results for hot-compacted Certran polyethylene fibre.

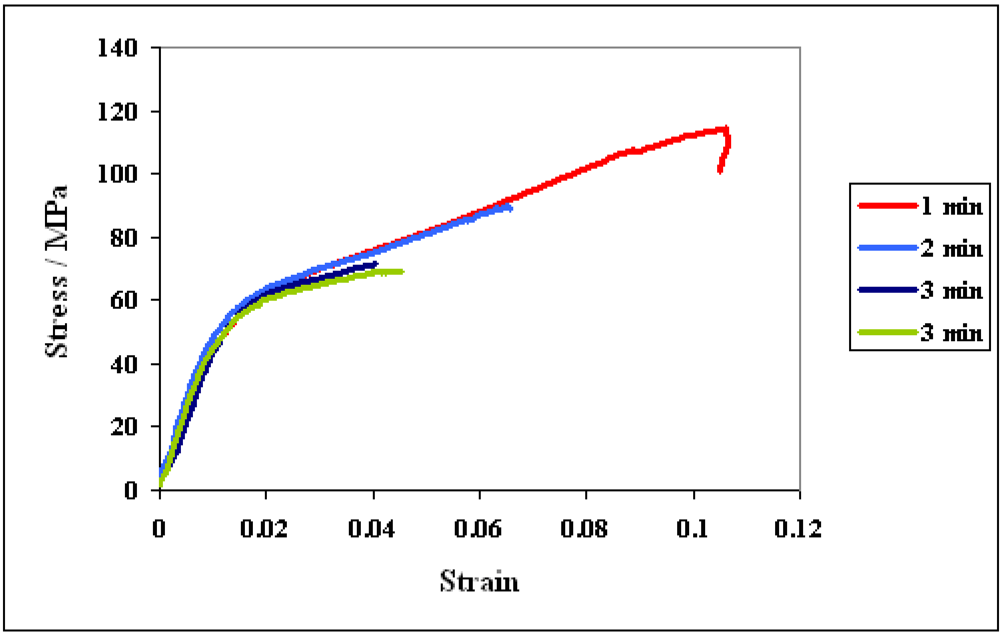

Figure 5: Typical stress strain curves for undried hot-compacted PET fibre.

Figure 5 shows large deformation stress strain curves in PET. Such curves are used to establish parameters such as the yield stress, strength and elongation to break. These results have been chosen to illustrate a disadvantage found in PET. They relate to samples produced from an oriented fibre phase in a plain weave arrangement. Four layers of cloth have been used with the usual compaction parameters but with different dwell times. In this case the cloth has not been dried before hot-compaction. The significant observation is that in undried PET the compaction time has a pronounced effect on the stress strain behaviour at large strains. As the compaction time is increased the strength and elongation to break are both reduced due to increasing hydrolytic degradation. The initial modulus and the yield stress are unchanged, although longer dwell times would be expected to have an impact on the latter. This detrimental effect can be removed by drying the cloth prior to hot-compaction, so it is not insurmountable although it does present cost challenges to commercial exploitation.

2.2.3 Dynamic mechanical behaviour

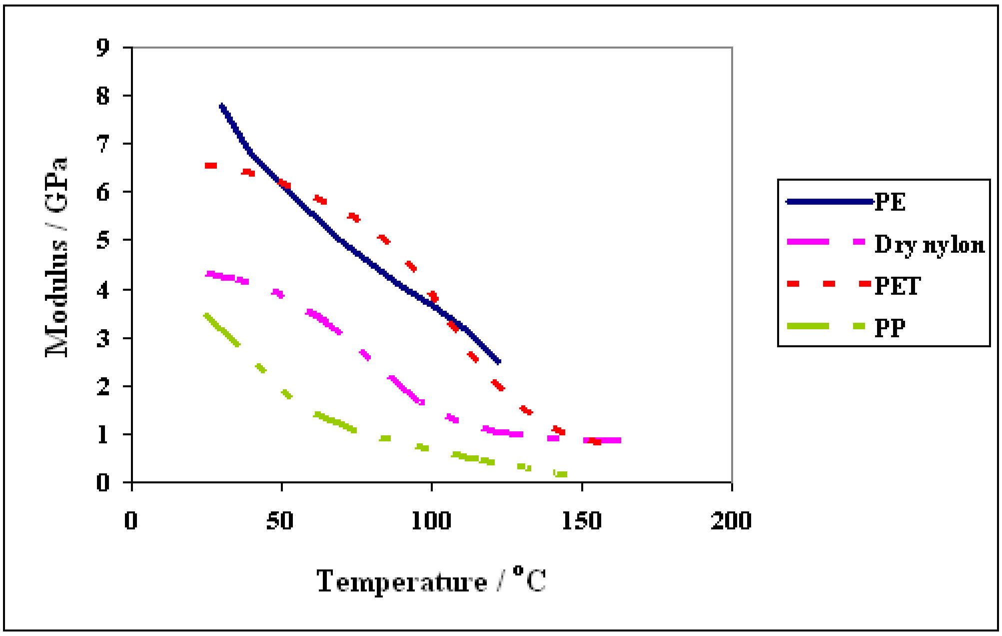

Figure 6: The variation in Young's modulus (from bending) with temperature in hot-compacted sheets of some common polymers.

When assessing the viability of novel hot-compacted products, it is important to examine mechanical behaviour over a range of temperatures. Figure 6 illustrates how the dynamic modulus varies with temperature for some potentially useful polymers, polyethylene, polypropylene, nylon and PET. As expected, all show a decrease in the modulus with increasing temperature. This dependence is strongly related to the position and strength of molecular relaxations occurring in the material. Thus, for example, the modulus of PET and PP falls significantly at temperatures of approximately 70°C and 10°C, respectively, and both are attributed to the onset of the glass relaxation. Reducing the strength of the relaxation, for example by increasing the crystallinity, or increasing the temperature at which it occurs, for example by adjustments to the molecular architecture, can reduce the extent to which or delay the temperature at which the modulus falls.

3. ASSESSMENT OF MATERIAL PROSPECTS

Polymer	Tensile Modulus / GPa	Tensile Strength / MPa	Elong / %	Peel strength N /cm	Compaction temp
Curv PP - with film	4.2	120	20	8	190
PE - with film	15	250	4.5	12	140
Dry nylon - without film	3.4	175	20	25	264
PET – plain weave with film	4.3	102	11.1	2.3	262
Mod PET – with film	8			4	215

Table I: Some property combinations obtained in hot-compacted samples.

The specific combination of properties that can be achieved in hot-compacted products of any specific polymer depends on factors such as the nature and mechanical properties of the oriented phase, the arrangement of the oriented phase, usually reflected in the nature of the weave, whether or not interleaved film is used and the specific hot-compaction conditions. Table I shows property combinations for some polymers that we have investigated. They do not necessarily represent optimum combinations but are presented as examples of what is currently achievable and as a template on which relative merits can be discussed.

3.1 The current market

The one material that is currently available commercially is polypropylene and is marketed as Curv®. It is used in the production of, for example, suitcases and clearly satisfies a market need. Table I shows results that can be produced in hot-compacted products using the grade of PP found in Curv®. The room temperature tensile modulus is reasonable (4.2 GPa) but, as can be seen from Figure 6, the decrease in modulus with increasing temperature is very significant so that the high temperature performance of this material is a limitation. For the present commercial applications of Curv® the high temperature performance is adequate and beneficial factors such as a relatively low compaction temperature and cost have led to commercial success.

3.2 Existing possibilities

Table I displays results from three materials we have been investigating as part of a current programme of work [4] namely PE, nylon and PET. Considering PE first, it is clear that there is a significant improvement over PP with respect to the modulus, strength and peel strength. The compaction temperature is lower than that of PP and hence will lead to lower processing costs. It is also noticeable, from Figure 6, that the modulus of PE is consistently greater than that of PP in the temperature range up to 120 °C, although the low melting point will limit this advantage to temperatures not much greater than this. These results have been obtained on sheets made from Certran fibre which is not commercially available. Hence the results in Table I show that PE can offer a potentially attractive alternative to PP although it is not currently viable because of the lack of availability of a suitable starting material. Nevertheless, the clear potential of this material, coupled with the benefits in terms of the processing window which can be achieved through the incorporation of interleaved film (Figures 3 and 4 above) is prompting further investigations.

Turning to nylon, the results in Table II relate to samples that have been prepared from dried nylon fibre and that have been kept in a dry environment prior to testing. The significant benefit of nylon is its very high peel strength. This is, however, offset by the seriously detrimental impact on the modulus of moisture, so that the values of modulus quoted in Table I and Figure 6 are not likely to be achieved in service, where most products would be exposed to a degree of humidity. Clearly, if products are required to function at temperatures above 150°C, Figure 6 does show that nylon becomes a potential candidate for hot-compaction.

Results for PET are also shown in Table I. These results relate to samples that have been prepared from dried fibre arranged in a plain weave using interleaved PET film. Comparison with PP shows a degree of similarity with the exception of the peel strength which is considerably less. It is also noticeable that the compaction temperature of PET is considerably greater than that of PP. The modulus results for PET can be improved by using a matt weave and omitting the interleaved film to produce compacted products with a greater fibre phase orientation arising from the smaller degree of crimp in the matt weave (compared with the plain weave) and a higher proportion of the fibre phase. Figure 6 illustrates the temperature dependence of the modulus in such a sample. The greater modulus shown by PET is not in itself the significant advantage of PET over PP because it would also be possible to improve the modulus of PP by altering the weave style. The significant advantage relates to the shape of the curves in Figure 6 with PET showing a much smaller sensitivity to temperature.

By themselves, the mechanical results in Table I and Figure 6 show that PE and PET offer significant advantages over the existing commercially available material. The advantages of nylon are limited to high temperature performance. A thorough assessment, however, must consider other material properties and factors. The following section takes a broader view of the problem and discusses material modifications which offer potential solutions.

3.3 Future developments

Table II lists some advantages and disadvantages of the four materials investigated here in relation to their suitability to the hot-compaction process. All can be hot-compacted to produce sheets which have enhanced mechanical properties but the choice of a suitable polymer for hot compaction depends on the full suite of relevant properties displayed by the hot-compacted products and the commercial costs which in turn are strongly dependent on processing costs. For PE we have shown that it is possible to produce compacted products with high modulus and strength when using a highly oriented fibre, Certran, as the starting material. The main physical disadvantage is creep performance and this would need to be considered when investigating possible applications. The main obstacle to progress with PE is the lack of availability of a suitable starting material. The clear success of Certran, the low processing temperature and the possibility of widening the processing window through the incorporation of interleaved film act as strong incentives to resolving this issue.

Material	Advantages	Limitations
PE	**Peel** **Modulus** **Strength** **Processing window** **Processing temperature** **Density**	**Flexural modulus** **Creep**
Nylon	**Peel** **Processing window**	**Modulus and strength (c.f. PP)** **Processing temperature** **Water sensitivity**
PET	**Strength (temp sensitivity)** **Modulus (temp sensitivity)**	**Peel** **Processing temperature** **Processing time / degradation**
Curv PP	**Processing temperature** **Processing window** **Impact strength**	**Modulus** **Strength**

Table II: Some property combinations obtained in hot-compacted samples.

The higher processing temperature of both nylon and PET would inevitably lead to increased production costs. If this were simply a matter of increased energy consumption it is possible that property improvements might be sufficient to offset this disadvantage in certain applications, but the problem is exacerbated by the fact that the processing temperatures for both nylon and PET are at the limit of, or greater than, what is currently achievable on commercial belt-presses. This poses a serious practical problem and under current conditions excludes nylon as a possible viable material. This limitation would also apply to pure PET but it is possible to obtain modified polyesters with lower melting points such that the processing temperature for these modified polyesters falls within the operating range of existing belt presses.

One modified polyester which we have used to produce hot-compacted products has been processed at temperatures close to 215°C. Some results for this material are shown at the bottom of Table I. The modulus of the starting material is about 25 GPa and that of the 4-ply balanced hot-compacted product is about 8 GPa. This value is less than half that of the original material, in part because the interleaved film represents about 25% of the sample. Nevertheless, this value represents a very reasonable level for a hot-compacted polyester sheet and the lower processing temperature and enhanced temperature performance of this material provide considerable optimism that materials such as these are viable materials.

4. CONCLUSIONS

A comparative assessment of the key properties of self-reinforced polymers has been undertaken for polypropylene, nylon and poly(ethylene terephthalate), based on small scale production. For each polymer some advantages have been identified, relating to such factors as temperature performance, room temperature mechanical properties and processability. Although the presently manufactured Curv® self-reinforced polypropylene has an excellent portfolio of properties for a range of applications, there are some performance advantages in other polymers which may open up further applications for the hot compaction technology.

ACKNOWLEDGEMENTS
We wish to acknowledge the support offered through a DTI funded programme [4] and the assistance of our collaborative partners in Futureplas. We would also like to thank Propex Fabrics GmbH for their cooperation in supplying materials.

REFERENCES

1. Hine, P.J., Ward, I.M., Olley, R.H. and Bassett, D.C., “The hot compaction of high modulus melt-spun polyethylene fibres”. *Journal of Materials Science*, Vol. 28, pp 316-324, 1993.
2. Hine, P.J. and Ward, I.M., “The science and technology of hot compaction”. *Polymer*, Vol. 45, pp 1413-1427, 2004.
3. Hine, P.J. and Ward, I.M., in “Mechanical Properties of Polymers based on Nanostructure and Morphology”., Taylor and Francis, 2005.
4. DTI funded programme www.futureplas.com