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Forming self-reinforced polymer materials

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9.1 Introduction

The aim of this chapter is first to provide an outline of the postforming methodology for self-reinforced composites, using as an illustration the materials produced by the Leeds hot compaction process, and secondly to describe examples of the present commercial applications of this new technology. This will be preceded by an introductory section introducing the hot compaction process and the self-reinforced composite materials produced by this manufacturing route.

The hot compaction technology was initiated as a research project in the IRC in Polymer Science & Technology at Leeds University in 1990. This led to a series of research programmes during the period up to 1995 when the commercial possibilities were recognised and a small spin-off company Vantage Polymers Ltd was set up, under the auspices of Leeds University. Professor I M Ward was Managing Director, Mr. Derek Riley Marketing Director and Dr. Peter Hine was a key member of the technical team. During the period 1995–2000, manufacture, postforming to produce real parts and detailed property measurements were undertaken, with the focus on hot compacted polypropylene which showed the greatest commercial potential. In 2000, full scale commercialisation was commenced by Amoco Fabrics GmbH (now Propex Fabrics GmbH). In this chapter, the achievements of all these three phases will be described, with particular emphasis on the requirements for successful forming of parts from hot compacted polypropylene sheet. The products are marketed under the trade name CURV®.

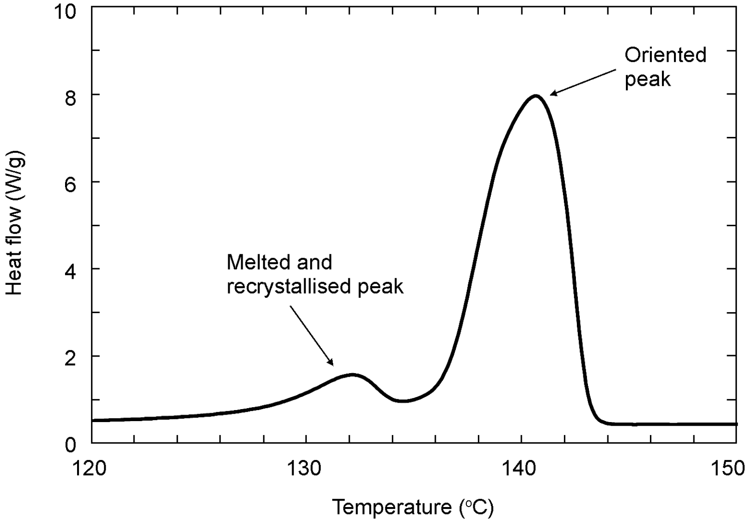
9.2 The hot compaction process

In a traditional polymer composite, a polymeric matrix is typically reinforced by a stiff ceramic fibre, more often than not glass or carbon. Recently, significant research has been carried out into the manufacture and preparation of a new class of polymer composites where *both* phases are polymeric. The reinforcing phase is usually an oriented polymer, with enhanced properties due to preferred molecular orientation and the matrix phase is usually an isotropic polymer.

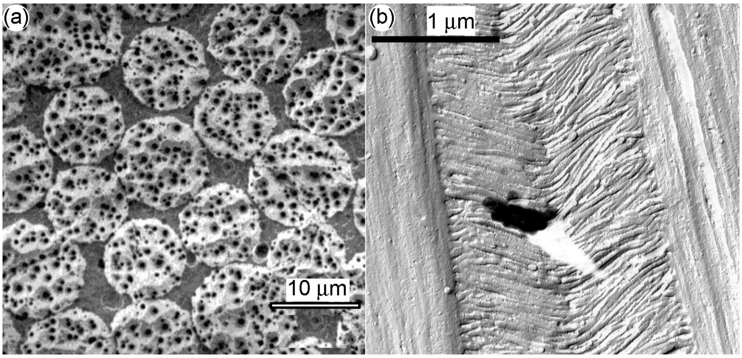
The production of all polymer composites, has been the subject of investigation by several researchers, using, in general, two discrete and different polymeric components. In a recent development, Peijs and his colleagues[1] have produced polypropylene composites from oriented tapes coated with a thin skin of lower melting point polymer, which can be melted and resolidified on cooling to form the matrix phase. This is not dissimilar from a very much earlier study, where Porter and his team[2] combined highly drawn polyethylene fibres with polyethylene polymer as the matrix, using the higher melting point of the fibres to ensure that the isotropic polymer could act as the matrix without melting the fibres. Other methods include film stacking,[3–5] powder impregnation,[6] solvent impregnation[7] and the use of a sudden reduction of pressure to induce melting in the matrix phase.[8]

The approach taken at Leeds, termed hot compaction, is different from those noted above in that it starts with only one component, an array of oriented fibres or tapes, most conveniently in the form of a woven fabric. Research over a number of years[9–11] showed that if this assembly is heated to a critical temperature, a thin skin of material on the surface of each oriented fibre or tape is melted, which on cooling recrystallises to form the matrix of the material.

The essential feature of the hot compacted self-reinforced composites is that they consist of two phases, both of identical chemical composition, an oriented fibre phase consisting of the central parts of the original fibre or tapes which have not melted and a matrix phase of melted and recrystallised material. This is illustrated very clearly in Fig. 9.1, which shows the DSC melting endotherm for



9.1 DSC melting endotherm for a compacted melt spun polyethylene sheet.



9.2 Etched micrographs from unidirectional PE fibres: (a) SEM picture of a transverse section of compacted fibres, (b) TEM picture of an interstitial lamellar region and its junction with adjacent fibres.

a compacted sheet produced from a parallel array of melt spun high modulus polyethylene fibres.

It can be seen that the melting peaks for the oriented fibre and the recrystallised isotropic matrix phases are quite distinct. Similar results have been obtained for other polymers, notably polypropylene, where the commercial exploitation has been concentrated, and polyethylene terephthalate. Our understanding of the structure of the hot compacted materials has benefited greatly from electron microscopic studies of permanganate etched samples, undertaken by Professor David Bassett and his colleagues at Reading University in a very valuable collaboration with the Leeds team. Figure 9.2 shows typical electron micrographs of etched samples of compacted unidirectional PE fibres. Figure 9.2a shows a SEM picture of a transverse section, and clearly shows the oriented fibres surrounded by a matrix of melted and recrystallised polyethylene. More detail of the recrystallised polymer is seen in Fig. 9.2b, which shows a TEM picture of a region between two polyethylene fibres. The picture shows that the 'matrix' polyethylene recrystallises epitaxially onto the remaining fraction of the oriented fibres.

The key variable in the production of these self-reinforced composites is the hot compaction temperature, which determines the proportion of melted material. Extensive experience has shown that to obtain satisfactory consolidation for compaction of fabrics, this should be about 25%, although for a unidirectional array this can be as little as 10%.

While the original research was carried out on unidirectionally arranged arrays of oriented fibres, the commercial materials are based around woven assemblies of oriented tapes, leading to more balanced in-plane properties. The mechanical stiffness of these compacted woven sheets can be calculated by assuming that these are two phase systems with continuity of strain between the oriented tape or fibre phase and the matrix phase. For a woven structure the composite modulus, $E_{\text{composite}}$ is then given by

$$\mathrm{E}_{\text{composite}} = \frac{V_f E_L}{2} + \frac{V_f E_T}{2} + (1 - V_f)E_m \qquad 9.1$$

where V_f is the volume fraction of the oriented phase, E_L, E_T are the longitudinal and transverse moduli of the oriented phase respectively, and E_m is the modulus of the matrix phase.

To a good approximation it can be assumed that $E_T = E_m$ giving

$$\mathrm{E}_{\text{composite}} = \frac{V_f}{2} E_L + \frac{(2 - V_f)}{2} E_m \qquad 9.2$$

Table 9.1 shows the results of these calculations for polyethylene, polypropylene and polyethylene terephthalate. It is important to note that whereas for the high modulus polyethylene fibre sheet the matrix stiffness makes a very small contribution to the overall stiffness, this is not the case for polypropylene and PET, where the modulus of the oriented phase is more modest. It is also of interest to note that for the woven PET multifilaments the measured modulus is lower than that predicted by the model. This is attributed to the effect of crimp that is present in the woven multifilament cloth, but which is much reduced when using woven flat tapes.

The matrix phase is also important in terms of its ductility which is relevant for large strain properties such as impact and thermoforming. In practical applications the use of woven fabric is essential, with the result that the matrix properties are very important as this dominates the strength between the layers (which can be measured using a peel test). Clearly such issues are also of paramount importance in considering successful postforming, as will be further discussed later.

Because of commercial importance, the hot compaction behaviour of woven polypropylene fabric has been studied in detail using a combination of mechanical tests, DSC and morphological measurements.[12–15] In the optimum compaction conditions there is epitaxial recrystallisation of the melted phase (similar to that seen with polyethylene – Fig. 9.2a), with the lamellae growing

Table 9.1 Predictions of in-plane compacted sheet modulus (based on the phase properties) in comparison with experimental measurements

	Polyethylene	Polypropylene	PET
Oriented element shape	Tape	Tape	Multifilament
Original oriented element modulus (GPa)	88.0	11.0	14.0
Melted matrix modulus (GPa)	0.51	1.2	2.8
Predicted compacted sheet modulus (GPa)	29.4	4.9	7.0
Measured compacted sheet modulus (GPa)	30.0	5.0	5.8

Using a volume fraction of 30 ± 5%.

out from the surfaces of neighbouring oriented tapes and any gaps on the structure are filled by row structures. With regard to the mechanical behaviour it is essential that there is sufficient ductility in the matrix phase for this to remain coherent up to the comparatively high failure strain (~15%) of the oriented PP tapes. This means that the molecular weight of the polymer has to be reasonably high (Mw > 300,000).

In two recent publications[14,15] the important parameters which determine the hot compaction behaviour of woven oriented polypropylene were identified by studies on compacted sheets produced from five commercial woven cloths based on four different polypropylene polymers. These cloths were chosen to define the boundaries of the key parameters which include the polymer molecular weight, the orientation of the tape, and comparisons of reinforcement with fibres or tapes and coarse and fine weave fabrics. A key result was the importance of the ductility of the matrix phase which requires that the molecular weight of the polymer should be moderately high, i.e. Mw > 300,000. There is also a requirement that for the best performance the stiffness and strength of the reinforcing phase should be high, which means choosing a polymer which can be drawn to a satisfactorily high draw ratio. Although low molecular weight polymers are often used for ease of draw, during the compaction process low molecular weight polymer will recrystallise to give a brittle material. Finally, with regard to the reinforcement shape (tape or fibre) and the weave style, the best combination of properties was found with flat tapes (avoiding the crimp usually present with woven fibre cloths) and a balanced weave style (plain weave). These geometry effects were monitored by determining interlayer adhesion using a T-Peel test (ASTM D1876) where samples 10 mm wide and 100 mm long were tested in an Instron at a cross-head speed of 100 mm/min, comparing both weft and warp directions. The morphological studies showed that the low molecular weight polymers tended to recrystallise as opposing transcrystalline layers, the junctions of which provided a low resistance path for peeling.

9.3 Commercial exploitation

To establish a baseline for commercial exploitation and evaluation of the properties of hot compacted PP, large sheets (~2 m × 1 m) were produced in an autoclave.[16] Following this, trials were undertaken to develop a continuous process using a double belt press at Hymmen GmbH, Bielefeld, Germany.[16] These trials led to the commercial operation of Propex Fabrics GmbH and the present CURV® products. Table 9.2 shows a comparison of the properties of self-reinforced PP sheet, isotropic PP sheet, random short glass fibre filled PP and PP sheet reinforced with continuous glass fibre, and indicates the strengths of self-reinforced polymers in general. It can be seen that self-reinforced PP sheet shows a very interesting combination of properties with a density

Table 9.2 A comparison of the mechanical properties of polypropylene based materials

		Hot compacted PP sheet (Curv®)	Isotropic PP homo-polymer	Random mat short glass/PP 40wt% fibre	Continuous sheet glass/PP 60wt% fibre
Density	kg/m^3	920	900	1185	1490
Notched Izod impact strength	J/m	4750 (20°C) 7500 (−40°C)	200	672	1600
Tensile strength	MPa	180	27	99	340
Tensile modulus	GPa	5.0	1.12	3.5–5.8	13
Heat deflection temperature	°C/455 kPa	160	110	154	155
	°C/1820 kPa	102	68		
Thermal expansion (@20°C)	10^{-6}/°C	41	96	27	21

Comparison data for other materials taken from www.matweb.com
Quoted values are averages of all commercially available grades
Compacted PP made on a pilot plant – www.curvonline.com

comparable to isotropic PP, tensile strength, tensile modulus and thermal expansion intermediate between the random short glass fibre and the continuous glass fibre PPs. Moreover, self-reinforced PP shows outstanding impact performance and it is particularly important that this is retained and even greater at −40°C where isotropic PP is brittle.

9.4 Postforming studies

Research to date indicates that the thermoformability of a self-reinforced polymer sheet lies between the two extremes of an isotropic polymer and a continuous glass fibre reinforced polymer. An isotropic polymer sheet can usually be easily formed by raising it to an elevated temperature above its glass transition, and stretching it into a mould of the required shape, often with the aid of a vacuum.[17] At the other extreme, a continuous glass fibre reinforced polymer composite sheet, where the fibre is inextensible, usually requires matched metal moulds, a significant forming pressure, and a temperature such that the matrix phase is melted and the fibres can rotate as required.[18] A self-reinforced polymer sheet falls between these two extremes because it is composed of oriented polymer elements and an isotropic polymer matrix. The oriented elements, while not inextensible like a glass fibre, are more resistant to stretching compared to an isotropic polymer, although the extensibility increases with increasing temperature.

In light of its commercial importance, the majority of the detailed thermoforming studies have been carried out on self-reinforced polypropylene sheet.

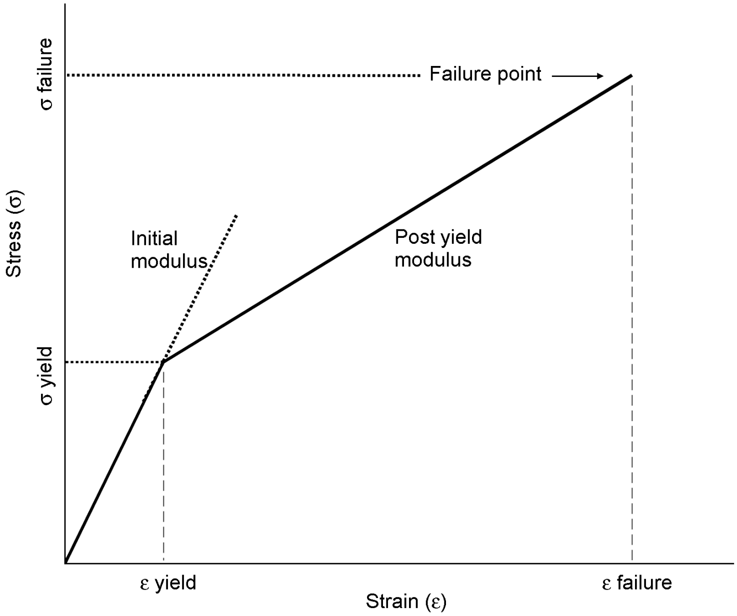
Three major programmes of work have been carried in this area: the first,[19] carried out at Leeds, used a combination of tensile tests and a spring-loaded hemispherical matched metal mould to assess the thermoformability over a range of temperatures and strain rates: in the second, which was part of an EPSRC sponsored programme 'DEPART', the group at Nottingham utilised a combination of picture frame tests and bias extension tests to examine thermoformability:[20] finally in the third, forming trials were carried out using a commercial glass mat thermoplastic (GMT) manufacturing line: the major findings in each of these three programmes will now be discussed.

9.4.1 Tensile tests and matched hemispherical mould experiments

The first programme of work, described in detail in reference 19, combined tensile tests at elevated temperatures with model thermoforming experiments carried out using a hemispherical, sprung loaded, matched metal tool installed inside a temperature-controlled cabinet. As was described above, the oriented elements have a significantly higher melting point compared to the isotropic matrix phase (and this separation is increased if the sheet is constrained), suggesting two potential thermoforming scenarios. Either thermoform at a temperature below the melting point of the matrix phase (for PP this is around 160ºC), where the sheet will behave as a homogeneous polymer, or thermoform at a temperature above the melting point of the matrix phase, where the fibres can then rotate as appropriate. The aim was to establish under what conditions of temperature, pressure and part design, the above two scenarios for forming could apply.

Hot tensile tests were carried out on samples cut from hot compacted PP sheets. Tests were carried out over a range of temperatures (140 to 170ºC) and a range of crosshead speeds (5 to 500 mm/min): temperature was found to be the most significant factor. The measured stress-strain curves all showed a similar shape, shown schematically in Fig. 9.3: an initial linear region up to a yield point at a strain of around 5%, followed by a strain hardening region of lower slope (termed the post yield modulus) up to failure. The post yield modulus is considered an important parameter as this indicates the resistance of the material to the degree of plastic deformation normally required for thermoforming. With increasing test temperature the post yield modulus was found to fall from 75 MPa at 140ºC to 40 MPa at 170ºC while the failure strain increased from 60% at 140ºC to 90% at 170ºC.

Thermoforming tests were carried out over the same temperature range using a spring-loaded hemispherical matched metal mould. The whole assembly was placed into a temperature controlled oven installed on an Instron tensile test machine, allowing the temperature of the mould and sheet to be accurately controlled and allowing the force during forming to be measured.

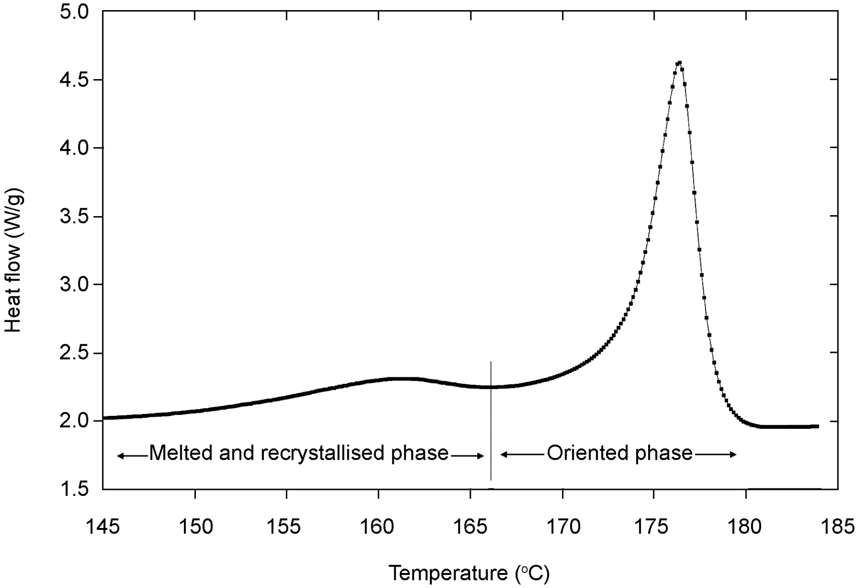


9.3 A schematic diagram of a typical stress-strain curve for hot compacted PP sheet.

For the first set of tests a fixed displacement of 10 mm was used, which resulted in partial forming of the hemispherical shape. The maximum forming force was found to decrease linearly with temperature: the maximum forming force was also found to show a linear relationship with the force measured at a similar strain in the hot tensile tests: this confirmed that a major component of the forming force is the resistance of the oriented elements to tensile stretching.

Sections taken from the thermoformed samples made at the different temperatures were examined for any signs of delamination, and a very interesting observation was made. At the lower temperatures of 140 and 150ºC no delamination was seen: at 160ºC a small amount of interlayer damage was seen, while at 170ºC no damage was seen. These results can be understood by looking at a typical DSC melting endotherm for hot compacted, self reinforced PP sheet shown in Fig. 9.4.

As was seen in the trace for polyethylene (Fig. 9.1) there are two peaks, a lower one associated with the melted and recrystallised material and a higher one associated with the oriented elements. At 140 and 150ºC, which is below the melting point of the matrix phase, the material behaves as a homogeneous sheet. At 170ºC, which is above the melting point of the matrix phase, the material will form more like a traditional fibre composite with a molten matrix: however, on cooling the matrix phase will recrystallise and bond the layers together again. At 160ºC, the matrix phase is not quite molten, but will be quite soft being so close



9.4 DSC melting endotherm for self reinforced PP sheet.

to the melting point. Significant interlayer shear could therefore break the matrix at this temperature, but because the matrix is not molten there is no mechanism for rebonding on cooling.

In a second set of experiments, the tool was completely closed, leading to a fully formed hemisphere: these tests were carried out both with a clamped sheet, and allowing the sheet to flow into the mould under a light pressure to restrict any wrinkling. Sections taken from the formed hemispheres indicated that if the sheet was clamped, then delamination often occurred. Conversely if the sheet was allowed to flow into the mould, then a well formed part with no delamination was the result.

From these observations it can be concluded that 160ºC is the worst choice for thermoforming self-reinforced PP sheet: for successful forming two alternative strategies can be proposed. If the strain is moderate, then the material should be formed at the highest temperature possible before melting of the matrix commences, 150ºC, and the sheet will behave as a homogeneous material. The material can be clamped if required. If a deeper draw is required, then the material should be formed at 170ºC, when the matrix is molten, allowing the oriented elements to rotate (and also stretch to some extent). Both approaches require matched metal tooling (or a pressure assist diaphragm) and in the second case the material should be under pressure during cooling to aid consolidation. Both forming regimes are also aided if the sheet is allowed to flow into the mould under the action of a small pressure to restrain wrinkling. However, as we will see in the next section, at 170ºC the sheet also has to be clamped to restrain shrinkage, so these two aspects have to be designed into the holding fixture.

9.4.2 Picture frame and bias extension tests

This second study built on the results of the experiments described in the previous section. Here the emphasis was on in-plane measurements of thermoformability using the picture frame and bias extension geometries (for a description and comparison of these two test geometries see refs 21 and 22). The picture frame consists of four equal length rails clamped over the sheet in a square configuration and hinged at the four corners.[23] If two opposing corners are then pulled apart, the square deforms into a rhomboid, forcing the clamped sheet to likewise deform. The force required to pull the frame is measured and the shear force can be determined. This test is normally used with either unconsolidated glass fibre based textile fabrics, or glass fibre reinforced composites where the matrix is molten, and is used to examine the effects of the weave style on formability (for example, the determination of the locking angle where the fibre tows can no longer rotate). The second geometry used in these experiments, which provided further information on the deformation mechanisms, was the bias extension test. Here a sample is cut from the sheet such that the main directions of the woven cloth are at ±45° to the direction of the applied force.

Following the work described above, three temperatures were used in these tests, 150, 160 and 170ºC. First the picture frame results. At 150ºC, the material was found to deform homogeneously in shear, with significant associated stretching of the oriented elements. At 160ºC the deformation was found to be more like a continuous fibre reinforced composite prepreg, while at 170ºC the deformation was very like a textile-type material (i.e., rotation of the oriented elements but no stretching). Two different weave styles were examined and there were significant differences in their formability, indicating that this is an important aspect which must be taken into account when assessing thermoformability. Another important result was the degree of shrinkage seen in the sheets at the different temperatures. At 150ºC, this was found to less that 1% so the sheet could be heated in an oven if required with no loss of properties or shape. However, at 170ºC, once the matrix was molten, the shrinkage could be as high as 30% (depending again on the weave style), indicating that for forming at this highest temperature the sheet has to be clamped. As would be expected, the measured shear force decreased as the temperature was increased, in line with the previous tensile tests. Also, minimal rate dependence was measured, also in line with the previous results.

The bias extension tests (carried out at 150 and 170ºC) showed the same trends as the picture frame tests, and if a normalisation approach was used[24] then the quantitative agreement was good between the two test geometries. In this test, the oriented elements were found to have extended at both temperatures, though more so at the lower temperature (6% at 150ºC and 4% at 170ºC). The locking angle was also found to depend on the temperature: at 150C this was 35º, whereas at 170ºC the locking angle was 65º. This confirms that for forming a shape with a deep draw or a complicated section requiring significant intra-ply shear, then a temperature of 170ºC will double the allowable shear deformation.

To summarise these results, the new ingredient in the forming of self-reinforced PP sheets, when compared to traditional composite forming, is that the reinforcing elements can be extended under certain conditions. Self-reinforced PP sheet has been shown to be a very low rate dependent material that is sensitive to forming temperature. The mode of material deformation depends both on the boundary conditions applied to the edge of the sheet during deformation and also on the relationship between the forming temperature and the melting temperature of the 'matrix' phase. If the sheet is relatively unconstrained, as in a bias extension test, the material will tend to deform through both pure shear and tow extension, irrespective of temperature. However, if the material is constrained, as in the picture frame test, below the matrix melt temperature the material will deform as a plastic sheet and undergo both shear and significant tow extension, whereas above the matrix melt temperature the material will deform more like a typical continuous fibre reinforced composite, i.e. no tow extension.

9.4.3 Forming trials using a commercial GMT production line

The aim of the third study was to transfer the results described above, generated under carefully controlled laboratory conditions, to a practical forming situation using a commercial GMT line. The line was composed of a conveyor belt fed set of heating ovens, placed in front of a compression press. Installed on the press were a pair of GMT metal moulds for producing an undertray part, similar to the one shown in Fig. 9.5a below. While the mould halves were not matched for the forming of a self-reinforced PP sheet, they did allow a series of thermoforming trials to be carried out. In these tests, the decision was made to form below the melting point of the matrix phase, as the sheet to be formed had to pass through the heating ovens unclamped. From the results described in the previous two sections it can be seen that the ideal temperature for the sheet to be formed at is 150ºC. However, there will be a delay between the heated sheet exiting the ovens and the time to place the sheet into the mould plus the mould closing time. It is therefore necessary to heat the sheet to a temperature above 150ºC to allow for this delay. The results above also showed that when the temperature approached 170ºC, and the sheet was unclamped, significant shrinkage occured. This behaviour therefore sets the boundaries for the processing parameters: heat the sheet as quickly as possible to a temperature not higher than 165ºC and then quickly transfer it to a mould, close the mould and thermoform when the sheet temperature had dropped to close to 150ºC.

To investigate the temperature profile of the sheet throughout the process, a data-logger was used which was able to travel through the oven with the sheet enclosed in an insulated box: data could subsequently be downloaded onto a PC. For the first experiments, the three individually controlled oven zones were set to a typical GMT profile of 222, 205 and 208ºC. The first zone is set to a higher temperature to get the sheet heated quickly, while the next two stages allow the temperature to approach the optimum value without overshoot, which is very important to stop shrinkage and loss of molecular orientation in a self-reinforced PP sheet. After a few scouting experiments, a dwell time of 30 seconds was used in each heating zone. On exiting the oven, the sheet temperature was found to be ~150ºC, cooling to 110ºC after 30 seconds. Raising the dwell time to 40 seconds increased the temperature on exit to around 160ºC.

For a more detailed experiment, six thermocouples were placed over the surface of a one metre square, 1.3 mm thick, sheet of self-reinforced PP. On exiting from the oven the average temperature was measured as 164 ± 2.5ºC: the sheet remained flat at this temperature suggesting that this is a good compromise between heating and shrinkage. After 45 seconds the temperatures were read again and gave an average of 116 ± 2.5ºC. This gave a fall of 48ºC, and a cooling rate of close to 1ºC/second for this sheet thickness. This suggests that a time of 15 seconds between exiting the oven and final tool closure would give the optimum forming temperature of 150ºC (in this process this time was 20 seconds with the results that the sheet would be at 145ºC for forming).

To assess the temperature that would be attained in the centre of a sheet, two 1.3 mm sheets were placed together and sent through the oven. Thermocouples were placed on the top and bottom surfaces and in between the sheets. The dwell time in each oven zone was increased to 50 seconds. On exit the temperatures were 152 ± 3ºC on top, 145 ± 3ºC in the middle and 148 ± 1ºC on the bottom (the oven heats from both sides). This suggests that for a 2.4 mm sheet, there would be a slightly lower temperature in the centre, although this could be better if the sheet was a single thickness of 2.6 mm, rather than two 1.3 mm sheets taped together. A longer dwell time could also be beneficial in allowing the centre to catch up.

In the final set of tests, the heated sheet was carried through to forming. This was carried out on a different forming line, using a four zone heating oven. In this case a dwell time of 42 seconds in each zone proved optimum (zone temperatures of 176, 264, 225 and 205ºC respectively). This gave an average sheet surface temperature of 159ºC on exit and an average surface temperature as the mould closed 20 seconds later of 145ºC. Good parts were made using these conditions with no sign of delamination or stress whitening, which was confirmed by subsequent mechanical tests including stress-strain measurements and puncture impact.

9.4.4 Final summary

The results from the three research programmes indicate two possible thermoforming strategies depending on the degree of deformation and complexity of part required. For reasonably simple shapes and low degrees of deformation (10% tensile extension, 30% shear deformation) then the best temperature for the sheet at the point of forming is 150ºC. At this temperature the shrinkage of the sheet is low so it can be heated unclamped in an oven if required. Matched tools are necessary for forming at this temperature. To obtain a sheet temperature of 150ºC at the point of forming requires heating the sheet to a higher temperature in an oven: a temperature of 165ºC is the highest that should be used before the onset of shrinkage: for a ~2 mm sheet this gives around 15 seconds for transfer of the sheet and mould closure. This thermoforming strategy is the most commonly used commercially.

For more complicated shapes then the best temperature is 170ºC, and matched tooling is again required. At this higher temperature, the tools must be closely matched to the final dimensions of the finished part taking into account the respective degrees of thinning in areas of higher deformation. This can make tool design challenging, but one solution is to have at least one half of the mould 'flexible' which is then able to conform to the thickness changes of the sheet, while maintaining forming pressure and consolidation after forming. At the higher forming temperature the material must be clamped to restrain shrinkage, although it is an advantage to allow it to flow into the mould during forming as this reduces the forming force and reduces inter-ply shear and delamination.

For both approaches, only modest thermoforming pressures are required.

Examples of commercial products, thermoformed using these two different strategies, are presented in the next section.

9.5 Key examples of commercial products

As discussed, self-reinforced polypropylene sheet may be postformed into parts over a reasonably wide temperature range at relatively low pressures. Taken in combination with the portfolio of mechanical properties and light weight this makes the material ideal for a number of manufacturing processes in a wide range of industries.

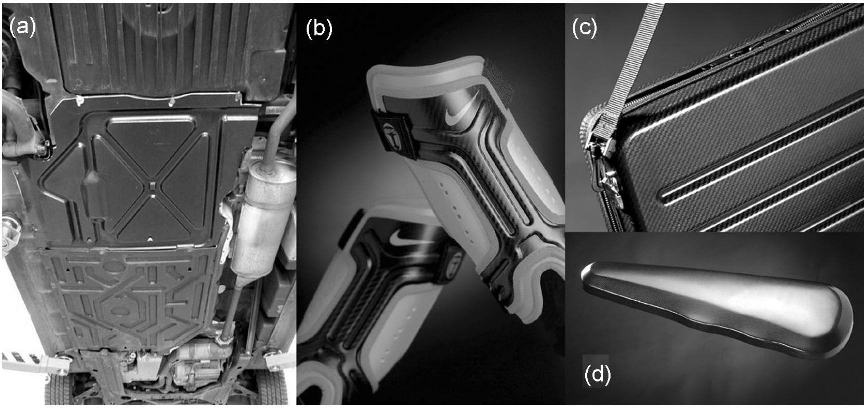
9.5.1 Automotive parts

One of the most interesting aspects of the behaviour of self-reinforced PP sheet is the high resistance to impact and abrasion, especially in view of the fact that these high values are retained at low temperatures. This notable property makes self-reinforced PP sheet an ideal material for automotive exterior components, especially under body shields. Such parts are subjected to very high levels of impact and abrasion, yet need to be lightweight and easily removed for maintenance.

Abrasion tests have been carried out by Daimler Chrysler,[25] comparing Curv® hot compacted PP sheet with three other materials – a conventional GMT with 20% glass fibre content, a 'heavy duty' GMT with 35% glass fibre and additional PET reinforcing fabric to improve its abrasion resistance and a natural fibre reinforced PP. The results indicate that hot compacted PP has significantly higher resistance to abrasion by grit and small stones than the glass fibre and natural fibre reinforced alternatives. In addition to ongoing vehicle trials, mechanical tests have been carried out to compare the mechanical properties of self-reinforced PP and GMT undershields. Such testing has shown that not only does self-reinforced PP exhibit higher impact and abrasion resistance than glass reinforced materials but the lower density allows weight savings as high as 50% in the finished part.

Figure 9.5a shows a hot compacted PP undershield installed on a vehicle. This part, thermoformed from a hot compacted sheet using matched aluminium tools, is surrounded by a number of similar GMT components, indicating the potential wide usage of replacement materials.

Under body components require no decoration and are left in their 'natural state'. However, visible exterior body panels often require painting to a Class A finish to match the rest of the vehicle. In common with other forms of polypropylene, self-reinforced PP has very low surface energy – typically 30 dynes/cm as produced. Nevertheless, standard flame treatment and plasma treatment methods are sufficient to raise the surface activity to enable the material to be painted using conventional painting systems. Flame treatment raises the surface activity to around 40 dynes/cm whereas two passes from a



9.5 Examples of commercial products from self-reinforced polypropylene sheet (Curv®): (a) automotive undershield (centre of picture) with original GMT components to top and bottom; (b) Nike (BPS Contour) soccer shin guards; (c) laptop computer case; (d) violin case.

hand held plasma gun can raise the surface activity to around 70 dynes/cm – a level which is maintained for more than seven days. Painting with an automotive primer and top coat following such surface preparation provides a Class A automotive finish which meets industry standards for temperature and humidity cycling, stone chip and adhesion.

In the case of vehicle interiors the competition from lower cost materials such as wood-filled PP is more intense. However, self-reinforced PP is already used in safety-critical areas such as air bag release mechanisms and impact-resistant seat backs where guaranteed performance over a wide range of temperatures is required. Furthermore, in combination with other materials, such as all-polypropylene laminates, self-reinforced PP is seeing applications in load floors and rear parcel shelves where stiffness at moderately high temperature tends to preclude the use of unreinforced polypropylene.

9.5.2 Sports protection

The combination of lightweight and outstanding impact performance makes hot compacted PP a candidate for sports protection. The first application to make use of this material was for a range of soccer shin guards launched onto the market in early 2003. The finished items are shown in Fig. 9.5b. These shin guards combine Curv® with a foam to produce a component which outperforms other candidate combinations. Manufacture of the self-reinforced polypropylene protective insert is achieved using unheated matched metal tools in a simple hydraulic press. Multiple sheets are heated prior to moulding in an air convection oven giving an overall cycle time per piece of less than 30 seconds.

9.5.3 Protective cases and luggage

Protective transportation cases for electronic devices, musical instruments, etc. have been manufactured in a wide variety of materials ranging from metals to wood coated with fabrics. Self-reinforced thermoplastic composites offer an ideal combination of light weight with high levels of impact resistance, moisture resistance and ease of manufacture. The material is easy to work and features such as hinges and fasteners can be included using conventional processing.

Figures 9.5c and 9.5d show two different types of case produced by low pressure compression forming. In both these applications a relatively high depth of draw is required which would be difficult to achieve by simple compression moulding of the sheet material. To overcome this these components are produced with the aid of a sprung clamp frame which allows the sheet to slip into the tool in a well controlled manner, eliminating creases and creating good definition with a relatively tight radius in the corners.

9.5.4 Safety shoe components

Besides having very high levels of impact resistance, self-reinforced polypropylene also exhibits exceptionally high compressive strength, in excess of 500 MPa, which results in a material with very high penetration resistance. The material does not possess high speed ballistic resistance but it is remarkably resistant to slow speed puncture as required for insoles in safety footwear. The only cost-effective alternative to self-reinforced polypropylene in this application is steel. Advantages of the thermoplastic composite solution include much lower thermal conductivity for greater comfort, non-metallic to prevent false alarms in metal detectors in airports and other places of work and, for certain applications, non-conductive (a special requirement in fire fighters' boots). Combined with an all-PP toe cap, capable of withstanding 200 joule impacts (an international standard) for the first time allows the manufacture of safety footwear without metals or glass.

9.5.5 Audio equipment

There are three key requirements of materials used to make audio cones for loudspeaker systems: the material must be resistant to moisture, it must have high stiffness/weight ratio and to prevent resonance it must have self-damping properties. Many different materials have been used over the years but all fail in at least one area. For example, paper cones can be made with high stiffness/weight but they are affected by moisture unless coated with a lacquer which then affects the damping qualities; carbon fibre and Kevlar cones are light weight, high stiffness, impervious to moisture but they have poor damping; injection moulded PP has excellent damping but it is not stiff enough to give a clear sound. Self-reinforced polypropylene is a unique material in that it meets all three requirements and for this reason is used in some of the highest quality hi-fi systems produced.[26]

9.6 Future developments

Hot compacted PP sheet was a natural choice for the initial exploitation of the hot compaction technology. However, in both the Leeds researches and in studies elsewhere, other polymers have been identified for possible commercialisation. As described above, the earliest researches were undertaken on polyethylene and in collaboration with Westland Helicopters it was confirmed that the very low absorption of electromagnetic radiation of this polymer is valuable with regard to radome covers.

Table 9.3 shows a comparison of the room temperature properties of hot compacted sheets produced from a very wide range of polymers. Polyethylene (PE) is exceptional in showing very high values for modulus and strength,

Table 9.3 A comparison of the properties of the optimum compacted sheet for a range of different polymer types

	PE Tensylon	PP Curv®	PET	PEN	POM
Oriented phase type	Tapes	Tapes	Fibres	Fibres	Tapes
Oriented phase arrangement	Woven	Woven	Woven	0/90	0/90
Compaction Temperature (ºC)	153	191	258	271	182
Oriented phase modulus (GPa) E_L	88	11	14	22	22
Matrix phase modulus (GPa) E_M	0.5	1.2	2.8	3.3	3.2
Initial compacted sheet modulus (GPa)	30	5	5.8	9.6	10
Compacted sheet failure strength (MPa)	400	182	130	207	280
Compacted sheet failure strain	2	15	10	6	6
Density (kg/m^3)	980	910	1400	1410	1420

reflecting the outstanding mechanical properties of the highly oriented fibres incorporated in the sheets. Polyethylene naphthalate (PEN) and polyoxymethylene (POM) also show significantly higher values of sheet stiffness and strength than PP, but it is in respect of the temperature performance of all these polymers that exciting prospects emerge. Considering Table 9.3 it is clear that PEN and POM are outstanding candidates for a new generation of hot compacted materials. Taking into account the likely cost of the compacted sheets, PET (polyethylene terephthalate) can also be seen as a very interesting possible polymer for the technology. However, a major point is that the postformability of all these materials has to be explored before it can be concluded that they show an adequate overall portfolio of properties for extensive commercialisation.

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