Single Polymer Composites Based on Polypropylene: Processing and Properties

Benjamin Alcock

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Abstract

Isotropic polymers lack sufficient strength and stiffness for many engineering applications. In order to improve these properties polymers can be filled with structural reinforcements such as glass or natural fibres. However, current major trends focus on simple monocomponent systems in an effort to reduce costs and increase recyclability. Composite systems, by definition, must employ at least two phases with different material properties. With the introduction of careful processing routes, it has been proven possible to create a fibrous, two phase composite, in which both are polypropylene.

Polypropylene can be melt spun and solid state drawn to give oriented tapes, and moduli of ~15GPa and tensile strengths of ~550MPa can be achieved. These tapes can then be oriented into sheets, either in the form of woven fabrics or unidirectional layers. These sheets form the reinforcing phase of a single polymer composite material. Such single polymer composites based on polyolefins can be produced by using a separate matrix impregnation route, but these are limited by relatively low volume fractions of reinforcement. Previous work executed at the University of Leeds showed that polymer fibres can be welded together by selective melting of the fibre exterior, but this method is limited by a small temperature processing window.

By using polypropylene tapes co-extruded with a copolymer skin, it has been shown that such tapes can be welded together at temperatures far below the melting temperature of the tapes, thus ensuring that thermal relaxation of the highly oriented polymer does not occur. The temperature processing window can be widened further by constraining fibres during heating. The optimisation of the drawing and structure of these tapes, together with an investigation of the static and dynamic mechanical properties, impact resistance and interfacial properties of composites formed from these tapes, are investigated in this thesis.
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Chapter 1

Introduction

To describe the development of an All-Polypropylene (All-PP) composite material, it is first necessary to describe the nature of polypropylene and the current alternatives to All-PP composites as engineering materials. Currently the global annual production of polypropylene is estimated to be 26 million tonnes (Brydson, 1999) and is the third greatest production of polymer after polyethylene and PVC. PP represents around 15% of thermoplastics produced, although this proportion has shown steady growth over the past few years. Polypropylene benefits from comparatively efficient polymerisation technology adding to an already cheap monomer, making polypropylene very cost competitive; polypropylene homopolymer pellets typically cost 1 €.kg⁻¹. Polypropylenes possess good mechanical properties such as high toughness, good impact and creep resistance and are relatively inert, meaning that they find many applications in the food packaging industry, as well as in automotive components, ropes, toys, carpets, and a diverse range of household goods. Polypropylene is also extremely versatile and processing routes include injection moulding, vacuum forming, extrusion, blow moulding and fibre spinning.

1.1 Polypropylene

Polymer materials are composed of large molecules formed of many (poly-) repetitions of small chemical units (-mers). In most cases, the entire polymer molecule will be made of many identical units. The nature of these simple units, together with the configuration within the polymer molecule, defines the macroscopic behaviour of the polymer. The focus of this research is on a particular family of polymers, polyolefins, the repeat unit of which is shown in Figure 1.1. The most simple polyolefin is polyethylene (PE), which was first polymerised, largely by accident, by Fawcett and Gibson in 1931 (Gedde, 1995). Initially, the production of polyethylene required high pressures, but the work of both Ziegler and Phillips, independently, provided new catalysis routes which led to the production of polyethylene at lower pressures. The research of Ziegler was developed further by Natta, who in 1954, developed a catalysis route which led to the creation of stereospecific polypropylene (PP). This has been subsequently titled Ziegler-Natta catalysis. Prior to this, atactic polypropylenes had lacked sufficient mechanical properties to be of commercial interest.
Unlike the ethylene monomer, the propylene monomer possesses a large methyl side group (see Table 1.1). This side group causes steric hindrance which distorts the molecule into a helical structure, unlike the linear structure of polyethylene. The position of the methyl side group determines the tacticity of the polypropylene molecule, which in turn affects the ability of the molecule to crystallise. In isotactic polypropylene, all the methyl groups exist on the same side of the molecule, and this regular structure permits a high degree of crystallisation. Typical commercial isotactic polypropylenes are approximately 95% isotactic (Brydson, 1999).

1.1.1 Bulk Modulus of Polyolefins

The properties of a non-oriented polymer are largely dictated by the properties of the polymer molecule, their arrangement and the load transfer mechanism between them. To determine the properties of the polymer molecule, typical bond strengths must first be considered (see Table 1.2). The polyethylene molecule, although linear does not possess loading in the C-C bond direction since steric hindrance gives the polyethylene backbone a zigzag conformation. The large methyl group of the polypropylene molecule leads to much greater steric hindrance and yields helical structure (see Figure 1.2). Polypropylene has much lower inherent stiffness than polyethylene, since the
helical structure can easily deform during axial loading, see Table 1.3. Although the carbon-carbon bond of the polymer backbone may possess high strength and stiffness, since this is not loaded directly in these polymer molecules, the ultimate stiffness of perfectly aligned molecules is limited by the modulus of the polymer backbone structure. However, thermodynamic and kinetic considerations favour crystalline regions linked together by amorphous regions, and so the molecules are clearly never loaded directly in the polymer axis. Instead, the properties of a bulk polymer are dictated by weak van der Waals interactions between the polymer molecules. For this reason, the typical modulus of bulk polypropylene is 1-2GPa, rather than 49GPa predicted for the polypropylene molecule.

Table 1.2. Dissociation energy of different bonds from *Alexander, 2001, Gedde, 1995

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy  [kJ.mol⁻¹]</th>
<th>Bond Length [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>600*</td>
<td>0.15</td>
</tr>
<tr>
<td>van der Waals</td>
<td>10</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 1.3. Calculated and measured values of chain direction moduli for polyethylene and polypropylene crystals. From Andrews, 1979

<table>
<thead>
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<th>Polymer</th>
<th>Theoretical Modulus [GPa]</th>
<th>Measured Modulus* [GPa]</th>
</tr>
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<tr>
<td>Polyethylene</td>
<td>182</td>
<td>240</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>49</td>
<td>42</td>
</tr>
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*Measured by X-ray diffraction

1.2 Improving the Mechanical Properties of Polypropylene

The low modulus of isotropic polypropylene means that it is unsuitable for many load bearing applications. In order to improve the stiffness of polypropylene, two main routes will be considered here. The first route is to improve stiffness by the introduction of foreign fillers, such as glass fibres, to create polypropylene composite materials. The second route is the exploitation of the inherent molecular strength by uncoiling the molecules and orienting them in the direction of loading (Carothers and Hill, 1932), so that the load is transferred by the stiff carbon backbone rather than by weak intermolecular bonds.

1.2.1 Polypropylene Composites

Composite materials are composed of two or more distinct phases which combine to give a “unique combination of properties” (Mazumdar, 2002). The continuous (matrix) phase is present to bind the reinforcing elements together and so effect load transfer. The reinforcement can be of any geometry (such as beads or flakes), but the scope of this research will be limited to popular fibre geometries with circular or rectangular cross sections. The degree of reinforcement that fibres contribute to a
composite will depend on the mechanical properties of fibre, the volume fraction of fibres present, the orientation of the fibres and the load transfer between fibre and matrix. Fibres are selected for their high mechanical properties, particularly stiffness and strength, and matrix compatibility. A high matrix compatibility will provide a strong interfacial strength and so allow load transfer from fibre to matrix to subsequent fibre.

Ease of recycling clearly favours uniform materials; the recycling of traditional composite materials is complicated by the combination of different materials that gives them their improved properties. Since individual polymer molecules have been shown to possess much greater stiffness and strength than seen in bulk polymer materials, the potential tensile properties of the molecule can be harnessed by the manipulating the molecules so that they become aligned in the direction of loading.

### 1.3 Orienting Polymer Molecules

PE and PP are semi-crystalline polymers. Highly ordered crystalline regions of the polymer molecule are embedded in amorphous regions. This model (Statton, 1959) has subsequently been developed and proven in numerous scientific papers. The degree of crystallinity depends on numerous factors including thermomechanical history, molecular weight and tacticity. These crystalline regions possess a greater density than the amorphous regions, and are much more resistant to deformation, since van der Waals attractions exist between closely packed, neighbouring lengths of molecule within a crystal, as described previously in this chapter.

The strength and stiffness of bulk polymers are insufficient for many applications, due to the random orientation of the polymer molecules but mechanical properties of the polymer can be increased by orienting these molecules in the direction of loading. This can be achieved by a range of methods and three of these shall be considered here: melt drawing, solution (gel) spinning and solid state drawing.

For the whole of this research, draw ratio, \( \lambda \), is defined as:

\[
\lambda = \frac{l_1}{l_0}
\]

Where

- \( \lambda \) = Draw ratio
- \( l_0 \) = Original (undrawn) length
- \( l_1 \) = Drawn length

#### 1.3.1 Melt Drawing

The most direct method to achieve orientation of the polymer molecules is to orient the molecules above the melting temperature, \( T_m \), by extruding a melt, since at these temperatures, molecules have a high mobility and so show little resistance to deformation. However, just as orientation is easily achieved in the melt, the orientation is easily lost, since molecular mobility at these elevated temperatures is very high. The molecular movement allows relaxation and increasing entropy
favours unoriented systems, so immediate relaxation during orientation reduces the drawing effect. By injection moulding high viscosity melts at temperatures just above the melting temperature, some orientation can be retained but this decreases with increasing melt temperature. Song et al., achieved a tensile modulus and tensile strength of 3.7GPa and 90MPa, respectively, for an injection moulded PP component compared to 1.2GPa and 32MPa, respectively, for an isotropic form of the same PP (Song et al., 1995). The melt drawing of larger molecular weight polymers is also a problem since the high melt viscosity of large molecular weight (>5 x 10^5 kg.mol\(^{-1}\) for PE) polymers leads to frequent blocking of the drawing die (Peijs et al., 2000) and also melt fracture (Lemstra and Kirschbaum, 1985). Melt drawing is the most common form of polymer processing method, although high degrees of orientation and the associated large increase in mechanical properties are not obtained (Bigg, 1988). A small degree of orientation can remain following melt drawing, and this can be used as a basis for further solid state orientation.

### 1.3.2 Solid State Deformation

Solid state deformation of semi-crystalline polymers is possible well below the melting temperature, but above the glass transition temperature of the polymer. Below the glass transition temperature, a lack of molecular mobility leads to very low strain to failure and so large deformations are impossible. During drawing above \(T_g\), the polymer is effectively loaded in tension and so initial drawing is easily achieved due to the weak intermolecular bonding between neighbouring molecules and sufficient molecular mobility. Orientation at these temperatures does not allow the immediate relaxation that is seen in melt drawing to occur, since the applied temperature is too low. Some molecular movement is required to facilitate orientation, and this leads to a temperature window to provide optimum drawability of the polymer; above this temperature window, relaxation occurs (as in melt spinning) and below this temperature window, insufficient molecular movement prevents drawing and leads to fibre breakage. The degree of crystallinity also effects the ability of a polymer to be drawn in a solid state deformation process since crystalline regions act as obstacles to molecular movement. The optimum drawing temperature has been shown to be above a second transition, \(T_\alpha\), (see section 1.1.5 of this chapter) at which temperature molecular movement within crystalline regions permit greater deformation and splitting of crystals which allows greater orientation in the drawing direction (Aharoni and Sibilia, 1979a, b). Therefore, in this temperature region, greatest molecular mobility of the entire structure can be expected with greatest retention of orientation during processing.

Solid state deformation of PP can be achieved in numerous ways, such as roll drawing sheets, die drawing, hot nip drawing, or by drawing through a hot oven. The simplest commercial route for the production of PP fibres or tapes is by drawing an extruded fibre through a hot oven. Tensile deformation is achieved by pulling a fibre through an oven with a greater speed than the fibre enters the oven. Roll drawn isotactic PP sheets have been reported with a tensile modulus of 20GPa and a tensile strength of 500MPa in the drawing direction (Burke et al., 1987). Similar studies (Yang et al., 1994; Bartczak et al., 2002b, a; Bartczak, 2002) also used roll-drawing of PP and yielded similar properties. Die drawing of polypropylene involves the pulling of a billet through a heated die (Taraiya et al., 1987; Taraiya and Ward, 1991; Chaffey et al., 1997; Ajji et al., 1998), and involves a large contact between die and billet. An advance on simple isothermal die drawing is the development of zone drawing, in which a billet is drawn through a die and then immediately through an annealing zone, instead of drawing from the die into ambient conditions. This allows the drawn
polymer to anneal and recrystallise at elevated temperature, although this is not normally necessary for PP (Takayanagi and Yamada, 1982).

In each case, the maximum drawability achieved by solid state drawing of semi-crystalline polymers drawn between \( T_g \) and \( T_m \) is limited by the presence of molecular entanglements. The maximum attainable draw ratio for PP is \( \lambda \approx 25 \), and a maximum tensile modulus is still around half the modulus of the theoretical maximum for PP (see Table 1.4). To create an ideal oriented polymer, molecular weight should be maximised to provide greatest molecular continuity in the loading direction. However, in practice, above a critical limit of molecular weight, \( 2M_e \), for the formation of entanglements, the number of molecular entanglements rapidly increases with molecular weight (Macosko, 1994).

<table>
<thead>
<tr>
<th>Process</th>
<th>Temp [°C]</th>
<th>( M_n ) [kg.mol(^{-1})]</th>
<th>Draw Ratio</th>
<th>Modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone Drawing</td>
<td>137</td>
<td>740</td>
<td>21</td>
<td>18</td>
</tr>
<tr>
<td>Roll-Drawing</td>
<td>160</td>
<td>3400</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Die Drawing</td>
<td>110</td>
<td>-</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Oven Drawing</td>
<td>110</td>
<td>400</td>
<td>27</td>
<td>22</td>
</tr>
</tbody>
</table>

Therefore, as molecular weight becomes very large, large numbers of entanglements limit the drawability of the polymer. In order to further align semi-crystalline polymer molecules, it is necessary to reduce the number of molecular entanglements. Drawability can be increased by reducing the molecular weight (Capaccio and Ward, 1973), but a reduction in molecular weight results in lower mechanical properties due to lower molecular continuity in the direction of loading. Thus, there are two conflicting effects on mechanical properties due to an increase in molecular weight: an increase in mechanical properties due to greater chain continuity and a decrease in drawability due to greater entanglement density, resulting in lower mechanical properties.

### 1.3.3 Solution (Gel) Spinning

In order to draw very high molecular weight polymers such as ultra high molecular weight polyethylene (UHMW-PE), the number of molecular entanglements must first be reduced. Smith and Lemstra reported a technique for reducing these entanglements by dissolving UHMW-PE in a solvent (decalin) to form a PE gel (Smith and Lemstra, 1979, 1980b, a). After dissolving in the solvent, the UHMW-PE molecules are mechanically disentangled by stirring; the presence of the solvent allows disentangling by lubrication, although molecular movement is aided by slight heating (Bastiaansen, 1991). The gel (typically \( \approx 99\% \) solvent by weight) is strong enough to be spun through spinnerets into fibres and then these run through a solvent extraction/quenching bath. Since the UHMW-PE used is polydispersed, the larger molecular weight polymer chains are more readily extensible and become aligned in the direction of drawing. In the solvent extraction bath, the remaining solvent is removed from the fibres and recycled. The crystallised fibre is then drawn in an oven to further increase the mechanical properties before being finally wound onto a bobbin (Peijs et al., 2000). The drawability of the gel spun UHMW-PE is much improved, when compared to melt spun UHMW-PE, as shown in Figure 1.3.
Gel spinning has been successfully applied to ultra high molecular weight polypropylene (UHMW-PP, \(M_w=4.4 \times 10^6\)), and drawing to \(\lambda=100\) achieved a tensile modulus of 40GPa and a tensile strength of 1.56GPa (Matsuo et al., 1986). The UHMW-PP was drawn in a two stage drawing process with initial deformation of \(\lambda=20\), and subsequent deformation to \(\lambda=100\). The strength of the resulting film approaches and even exceeds theoretical values for the tensile strength of the polypropylene molecule, while the tensile modulus is close to the theoretical value (see Table 1.3) (Samuels, 1970). The effect of molecular weight distribution and drawing temperature on mechanical properties of oriented gel spun UHMW-PP has also been investigated, also using a two stage drawing process (Flood and Nulf, 1990). The effects of these parameters were reported as small, with tensile modulus increasing with molecular weight distribution and decreasing with draw temperature. The increase in modulus due to molecular weight distribution was attributed to an increase in crystal lamella thickness. The decrease in modulus due to increasing drawing temperature was attributed to increasing relaxation when drawing at higher temperatures.

\[\text{Figure 1.3. Maximum draw ratio vs. molecular weight for solid state drawn and gel spun polyethylene fibres (Lemstra and Kirschbaum, 1985)}\]

UHMW-PP is much less suited to gel spinning than UHMW-PE, since the lower stiffness of the PP molecule limits the maximum modulus of an optimum gel spun UHMW-PP fibre. In addition to this, the presence of the methyl group on the PP molecules results in a much greater crystallisation time, rendering the entire fibre spinning process ‘impractically slow’, although the recent addition of nucleating agents has dramatically reduced this time to within an industrially feasible time scale (Kristiansen et al., 2003). It is clear that since drawability and polymer microstructure depend on thermomechanical history, a careful combination of processing parameters must be employed during the orientation of a semi-crystalline polymer to optimise mechanical properties.
1.4 Single Polymer Composite Production

From the above, it is clear that there are two viable routes to increase the mechanical properties of polypropylene. Firstly, fillers or fibres can be added to PP to produce PP matrix composites, and secondly the properties of PP can be improved by molecular orientation achieved by drawing. The most common method to improve mechanical properties is through the addition of a filler such as talc or glass fibres. However, PP composites with foreign fillers suffer from reduced recyclability since the main obstacle for recycling composites is the separation of fibre and matrix, each of which have very different recycling requirements. This problem can be reduced or removed by using similar or identical materials for both fibre and matrix. Polymers are already commonly used to form the matrix phase of composites, and can also be drawn to yield high strength and high modulus fibres, but several studies have also investigated the use of polymers for both fibre and matrix phase of the same composite. This is not so straightforward because most traditional composite processing routes cannot be applied, and so novel methods have been devised to combine similar polymers. Ultimately, because these composites can be entirely thermoplastic, recycling is simplified to melting of the composite and reprocessing.

For the production of 1-dimensional products such as high modulus fibres and tapes, molecular orientation by drawing is suitable. However these high mechanical properties in one direction need to be transferred to a three dimensional product. Parallels can immediately be drawn between highly oriented polymers and composite materials, if the highly oriented polymer chains are considered as the reinforcing phase of the composite, and the remaining unoriented chains as the matrix phase. For example, a roll drawn sheet can be considered a unidirectional composite laminate (Tate and Perrin, 1988; Sinclair and McCammon, 1991; Sinclair et al., 1992). The bonding of stacks of oriented PP films was described (Lee and Schultz, 1985), with emphasis on the relative ease of achieving high mechanical properties through drawing of PP films, but the difficulty of retaining these properties by stacking into a three dimensional material. Layers of roll-drawn PP sheets were later successfully bonded together by using electromagnetic induction bonding, and this research showed that an excellent bond could be achieved between high strength PP sheets with a very small loss in tensile properties (Zach et al., 1989). In order to attain a direct comparison with fibre reinforced polymer composites, polymer fibre/polymer matrix composites were investigated.

Single polymer composites based on oriented PE fibres were first described in the mid-1970s (Capiati and Porter, 1975). In order to employ the high mechanical properties of polyolefin fibres, numerous investigations were conducted to combine high modulus PE or PP fibres with a similar matrix. Most early studies concern PE since the high theoretical modulus of a linear PE molecule (~250GPa) is much greater than the stiffness of the helical PP molecule (~43GPa) (Matsuo et al., 1986; Peijs et al., 2000). This molecular modulus ultimately limits the maximum modulus achievable in a fibre of either material, and so higher properties are achievable with PE fibres, and these were the most attractive polymer fibres for initial research. PE is widely cleared for food and medical use, and increasing mechanical properties by self reinforcement does not affect this as the addition of ‘foreign’ reinforcements might. This means that ‘All-PE’ composite materials are interesting for many applications, not least medical (Megremis et al., 1999). Mosleh et al., have investigated All-PE composites and found their biocompatibility and mechanical properties well suited to prosthetic wear surface applications (Mosleh et al., 1997). The lower molecular stiffness of PP due to the helical molecular structure means that there is less potential to construct very high
modulus fibres using PP, and this is reflected in the smaller scope of research into ‘All-PP’ composites. However, the lower glass transition and melting temperature of PE mean that creep at room temperature can be problematic and maximum usage temperature is lower than that of PP, which also benefits from a slightly lower price and density.

### 1.4.1 Traditional Impregnation Methods

The main difficulty of combining similar polymers in this manner is to retain the properties of the oriented polymer molecules in the final composite, since relaxation of highly oriented fibres readily occurs during heating (Bastiaansen and Lemstra, 1989). Initially, most studies focussed on traditional routes to create thermoplastic composites, such as melt, powder or solution impregnation of multifilament yarns.

The combination of similar polymer grades by exploitation of different melting temperatures, opens up many routes for the production of single polymer composites. The creation of single polymer composites based on PE was first suggested by Porter and co-workers in the mid-1970s (Capiati and Porter, 1975; Mead and Porter, 1978), by exploiting the difference in melting temperature of HDPE fibres and conventionally crystallised LDPE. A later publication described the presence of a transcrystalline zone surrounding the HDPE fibre (He and Porter, 1988) in these composites. The interfacial properties of composite systems are particularly important in short fibre composites, and this was investigated (Ajji et al., 1992) using short fibre UHMW-PE fibres in a LDPE matrix. In this case, composites were prepared by mixing the UHMW-PE fibres (T_m=147°C) at ~130°C in a LDPE melt (T_m=120°C). Mechanical properties obtained showed an efficiency equivalent to the UHMW-PE fibres to Kevlar fibres in the same matrix, and so UHMW-PE fibres were deemed a suitable alternative to Kevlar fibres, in this LDPE matrix. However, because this was a discontinuous fibre composite with relatively low fibre volume fractions, mechanical properties of the composite system were quite low. Short fibre composites using UHMW-PE fibres in a HDPE matrix, have been created by placing random fibres between two HDPE sheets (Stern et al., 1996b). This system was then consolidated by heating above the T_m of HDPE and applying pressure. Using this method, larger fibre volume fractions were achieved but similar mechanical properties were obtained.

UHMW-PE fibres have been combined with a LDPE matrix using a dry powder impregnation technique (Chand et al., 1993). UHMW-PE fibres were pulled through the LDPE powder in a fluidised bed, and then through an oven to melt the LDPE powder on the surface of UHMW-PE fibres. Because the melting temperature of UHMW-PE fibres (T_m>148°C) is greater than that of lower density PE, the LDPE powder can be melted by heating above the T_m of LDPE while the UHMW-PE fibre retains most of its original mechanical properties. Using this method, composite tapes were formed with a high retention of the original stiffness of the fibre. The impregnation of UHMW-PE fibres with a HDPE powder suspended in propanol has also been reported (Lacroix et al., 1999). The fibre bundles are pulled through the suspension and HDPE particles are trapped between the fibres. The suspandant can then be dried off, leaving a combination of HDPE particles amongst a bundle of UHMW-PE fibres. Again, these can be consolidated by exploiting the difference in melting temperature between the PE grades. This process could theoretically be applied to the dry powder impregnations described by Chand et al. to make larger composite components, although this is not discussed.
1.4.2 Hot Compaction of Single Polymer Composites

A novel method for the preparation of single-polymer composites, without the need for a separate matrix material has been created at the University of Leeds (Hine et al., 1993). Initial studies used high modulus, melt-spun PE fibres aligned in a mould and placed in a press; heat and pressure were subsequently applied. By carefully controlling the temperature applied, it was seen that the exterior of the fibre could be melted and with the simultaneous application of pressure, this molten PE flows to fill the interfibrillar voids. DSC studies suggested that after melting the fibre exterior, when the temperature is reduced, the molten PE crystallises on the remaining fibre to form a matrix phase binding the fibres together. This is shown schematically in Figure 1.4.

![Figure 1.4. Schematic of the hot compaction process](image)

By carefully controlling the processing parameters, up to 90% of the tensile modulus of the fibre has been retained in a PE/PE composite, but only by using a very small optimum processing window (139°C ±1°C) (Hine et al., 1993). A sharp decrease in longitudinal modulus and an increase in transverse modulus are seen on either side of this optimum compaction temperature as at higher temperatures, fibre properties begin to be lost by fibre relaxation. The transverse strength increases with compaction temperature, ultimately reaching the strength of isotropic PE when all orientation is lost. This processing window is somewhat larger when applied to gel-spun PE fibres, but in this research the superior mechanical properties of the gel-spun fibres could not be retained on compaction, and the resulting composite has similar properties to compacted melt drawn PE fibres (Yan et al., 1997). The hot compaction process was subsequently successfully applied to alternative grades of UHMW-PE (Hine et al., 2001), and PET (Rasburn et al., 1995), PMMA (Wright et al., 1996; Wright et al., 1999) and PP (Abo El-Maaty et al., 1996) fibres, in each case using a melted part of the fibre to act as the matrix. Because of the continuity between the fibre phase and the newly crystallised matrix phase, an excellent interfibrillar adhesion is seen in each of these cases. However, there is a fine temperature balance between melting a sufficient volume of the fibre to provide interfibrillar adhesion and melting an excessive volume of the fibre leading to a lower volume fraction of reinforcing fibre (Kabeel et al., 1994).

In early research focusing on hot compacted PP (Abo El-Maaty et al., 1996), a retention of only ~55% fibre properties was measured in the final composite, compared to ~90% for PE. Further research by the same group (Hine et al., 1998; Teckoe et al., 1999; Jordan et al., 2003; Hine et al., 2003), used PP tapes instead of PP fibres. Using a tape geometry PP, as well as PE
(Hine et al., 2001), was seen to be preferential to circular cross section fibres as the reduced thickness of the tape led to a lower crimping in the woven fabric, and so a more efficient reinforcement. Figure 1.5 shows an etched cross section of a hot compacted PP composite specimen, in which the boundary between three tapes is clearly visible, as well as the melted and recrystallised ‘matrix’ phase.

![Etched cross section of a hot compacted PP composite](image)

*Figure 1.5. An etched section through a hot compacted PP composite compacted at 182°C (scale bar = 10µm)*  
*(Hine et al., 1998)*

Figure 1.6 shows experimental results (Hine et al., 2003), which show the effect of compacting an PP/PP composite at temperatures around a proposed optimum, in this case 187.5°C. The optimum temperature was chosen because it yielded composites with the best combination of interfacial strength and tensile properties. Although greater interfacial strength could be achieved by using a greater compaction temperature, this resulted in a decrease in tensile properties due to thermal relaxation and excessive melting of the reinforcement. It is clear that a change in processing temperature of just a few degrees leads to a big decrease in longitudinal mechanical properties of the composite.

In order to understand the behaviour of polymer fibres in these processes, numerous studies have been performed analysing the structure of single polymer composites by SEM (Olley et al., 1993; Kabeel et al., 1994; Abo El-Maaty et al., 1999) and DSC (Hine et al., 1993). It was proposed (Kabeel et al., 1995), that during hot compaction, certain unstable regions within the interior of a PE fibre begin to melt at the same time as the exterior of the fibre. Thus as the exterior of the fibre is melting to form adhesive bonds, the interior of the fibre is already losing its molecular orientation. This further limits the size of the temperature processing window.

The interfacial properties of UHMW-PE composites have been investigated (Cohen et al., 1996; Cohen et al., 1999), and it has been suggested that there is an improvement of adhesion in PE/PE composites by pre-treatment of UHMW-PE fibres. This pre-treatment is the soaking of the fibres in an UHMW-PE/tetralin solution. The solution swells the fibre exterior and leads to the creation of a ‘brush layer’ composed of unoriented molecules radiating out from the fibre surface. These
molecules crystallise on removal from the solution into an intermediate radial structure which increases fibre-fibre bonding during subsequent consolidation.

**Figure 1.6. The effect of processing temperature on the tensile properties of hot compacted PP tapes**  
(Hine et al, 2003)

The effect of the morphology of this transcrystalline zone of PE-PE composites has also been reported separately (Stern et al., 1996a) and an increase in mechanical properties has been attributed to an increased transcrystalline zone (Levitus et al., 2001). An increase in mechanical properties has been reported following plasma treatment of UHMW-PE fibres (Rochette et al., 2000), but the increase in fibre-matrix adhesion was attributed to the surface chemistry of the fibre and there was no definite correlation between the surface chemistry and the transcrystalline zone morphology.

Since there are many routes to produce single polymer composites, the efficiency of various processing methods for unidirectional PE-PE composites is illustrated in Figure 1.7 to determine the optimum production method. The tensile modulus of these composites is given by $E_c$, in equation 1.2.

$$E_c = (1 - p)[E_f (V_f - \alpha) + E_m (V_m + \alpha)]$$

Where

- $E_f$ = Tensile modulus of the fibre
- $E_m$ = Tensile modulus of the matrix
- $V_f$ = Volume fraction of the fibre
- $V_m$ = Volume fraction of the matrix
- $\alpha$ = Volume of fibre lost during processing
- $p$ = Modulus loss coefficient of fibre
The matrix phase in each of these composites is unoriented, and so should suffer no loss in properties, but there may be some loss in fibre volume if consolidation occurs near the melting temperature of the fibre. This melted fibre will contribute to the matrix phase and so that:

\[ V_f + V_m \equiv 1 \]  \hspace{1cm} 1.3

Since thermoplastic fibres such as oriented polyethylene are very sensitive to thermal relaxation, it is possible that a loss in fibre modulus will be seen well below the melting temperature of the fibre (see Chapter 2). To account for this a modulus loss coefficient, \( p \), is introduced for the fibre, which describes the decrease in modulus to relaxation of the fibre. However, in the case of an ideal processing route, no thermal relaxation of the fibre occurs, so:

\[ p = 0 \]

Also, in the case of hot compaction, some fibre must be lost in order to provide the matrix phase. To preserve tensile properties in an ideal composite, the minimum fibre is lost to provide bonding between the fibres, so:

\[ \alpha \to 0 \]

Then equation 1.3 becomes

\[ E_c = k(E_f V_f + E_m V_m) \]  \hspace{1cm} 1.4

This is the classic ‘rule of mixtures’ for unidirectional composite systems, although the modulus of isotropic PE is very much smaller than the PE fibres, the contribution of the matrix phase to the composite can usually be ignored. In Figure 1.7, \( k \) multiplied by the initial fibre volume fraction is plotted against the initial volume fraction of fibre.

\[ k = f(\alpha, p) \]  \hspace{1cm} 1.5

This factor, \( k \), describes the percentage of fibre modulus retained during processing, and so describes the loss of fibre modulus due to molecular relaxation, and also a loss in fibre volume due to melting. An ideal composite would suffer no loss of mechanical properties due to consolidation, and so for the ideal composite, \( k = 1 \). The percentage of fibre modulus retained, can be determined from the proximity of the data to the ideal ‘rule of mixtures’ line. Of course, two effects are combining to decrease the performance of the composite: thermal relaxation of the fibre, \( p \), and melting (so physical loss) of fibre, \( \alpha \).

Since the processing routes involve consolidation by heating, it is expected that some relaxation of fibre is likely in all processing routes. While processing PE/PE composites by combining PE fibre/PE film (Mead and Porter, 1978; Levitus et al., 2001) may have greater efficiency (i.e. the highest original fibre properties retained), the presence of this PE film will mean that very high fibre volume fractions are not possible, and so ultimate composite moduli are limited. PE powder impregnation of PE fibres (Lacroix et al., 1999) is shown to have poor efficiency, and the addition of
the lower fibre volume fractions make this route unattractive. With both film stacking and powder impregnation routes, it is likely that with increasing fibre volume fraction, matrix impregnation becomes more difficult during consolidation. This may explain the increasing deviation from the rule of mixtures prediction with increasing volume fraction fibre of fibre and film stacking production methods.

Figure 1.7. The efficiency factor, k, of various unidirectional All-PE composite processing routes. Certan® is a melt spun PE fibre ($M_w=150$ kg mol$^{-1}$) manufactured by Hoechst Celanese, USA, Dyneema® is a gel spun UHMW-PE fibre ($M_w=1300$ kg mol$^{-1}$) manufactured by DSM, Netherlands, and Tensylon® is a gel spun UHMW-PE tape manufactured by Synthetic Industries, USA

Processing PE/PE composites by hot compaction (Hine et al., 1993; Yan et al., 1997; Hine et al., 2001) also showed a lower efficiency than fibre/film stacking, but because preconsolidation fibre volume fraction is 100% for hot compacted composites, actual properties of the final composite are much greater. Recalling that consolidation by hot compaction occurs by a melting of fibre, a reduction in fibre volume fraction is clearly required to make a coherent composite. It is clear from Figure 1.7 that hot compaction is the optimum processing route to manufacture PE/PE composites, although it is not clear what proportion of the decrease in mechanical properties is due to thermal relaxation of the fibres or actual melting of the fibres. Although Figure 1.7 concerns PE/PE composites, these considerations are also true of all semi-crystalline polymers and it can be safely assumed that these would also be true of PP/PP composites.

Interesting alternatives to single polymer composites are self-reinforced cellulosic composites (Matsumara et al., 2000). Here natural fibres are treated to plasticise the exterior of natural fibres, such as wood pulp fibres or sisal, which become thermoplastic. These fibres now have a skin/core structure with the stiffness of a fibrous the core with a deformable thermoplastic coating. By applying a processing route similar to hot compaction, this thermoplastic coating is melted into a matrix producing sisal/sisal composites possessing moduli >3GPa (Lu et al., 2003). Because these
composites are totally biodegradable, disposal is easy although this low stability may limit their application.

1.5 Scope of this Research

The methods for preparing single polymer composites can be classified into two groups:

(i) combination of a discrete fibre and matrix by exploiting the difference in melting temperature of two grades of polymer, *and*
(ii) hot compaction of fibre bundles to selectively melt fibre exterior in order to form a matrix phase.

Both of these methods are viable but have inherent limitations that reduce their viability; combining fibre/film or fibre impregnation is limited by *low fibre volume fractions*, while using a hot compaction route is complicated by a *very narrow temperature processing window* (see Table 1.5). The aim of this research is to develop a route to produce single polymer composites based on polypropylene by adopting the high efficiency of combining polymer grades with the high fibre volume fraction achievable by using hot compaction; a new processing route is proposed that takes the benefits from each of these routes.

<table>
<thead>
<tr>
<th>Consolidation Route</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre and Film Stacking</td>
<td>• Wide temperature processing window</td>
<td>• Poor matrix distribution at high $V_f$</td>
</tr>
<tr>
<td>Powder Impregnation</td>
<td>• Independent material choice for fibre and matrix</td>
<td></td>
</tr>
<tr>
<td>Melt Impregnation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hot Compaction</td>
<td>• Perfect matrix distribution</td>
<td>• Narrow temperature processing window</td>
</tr>
<tr>
<td></td>
<td>• Single polymer grade</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Fibre/matrix continuity provides excellent bonding</td>
<td></td>
</tr>
</tbody>
</table>

1.6 The Use of Constraining and Co-extrusion

It has been reported (Bastiaansen and Lemstra, 1989) that high modulus polyolefin fibres could effectively be ‘overheated’ above their melting temperature by constraining the fibre, i.e. physically fixing the fibre ends. To allow relaxation of a highly oriented polymer fibre, a macroscopic decrease of length in the drawing direction must occur. Physically constraining the fibre ends prevents shrinkage and thus prevents the molecular reorientation which causes the loss of modulus and, ultimately, a return to the isotropic state. It is possible to use this overheating by constraining process to create an ‘artificial’ difference in melting temperature between two structures of the same grade polymer, by constraining one but not the other. Figure 1.8 shows two DSC curves, one taken
from the melting of a constrained fibre, and the other from an unconstrained fibre. There is a clear endothermic peak at the melting temperature of each fibre, and this occurs at 160°C for the unconstrained PP fibre, but around 190°C for the constrained fibre.

This ‘overheating’ can be applied to further expand the temperature processing window of the hot compaction methods described above, and is probably already affected by the application of lateral pressure by the press. This artificial expansion of the temperature processing window could be applied to many of the initial studies aimed at combining different grades of PE, but is most interesting for combining the same grades of a polymer. This constraining method has recently been successfully applied to investigate the feasibility of creating a composite of high modulus PP fibre within a matrix of the same grade of PP (Loos et al., 2001), and model composites have been prepared by using this constraining route to produce a single-fibre micro-composite model. An optical micrograph is shown in Figure 1.9, in which a PP fibre can clearly be seen consolidated in the middle of a mass of isotropic, spherulitic PP.

Our studies have investigated alternative methods to further increase this temperature processing window. This new development uses high modulus PP homopolymer tapes which are co-extruded with a coating of a PP copolymer (Peijs, 2003). This PP copolymer has a lower melting temperature \((T_m \approx 140^\circ C)\) than the PP homopolymer \((T_m \approx 160^\circ C)\). These co-extruded tapes can then be oriented in a mould and heated to above the melting temperature of the copolymer, while constraining by the application of lateral pressure in a hot press leads to a temperature processing window of 30°C. This pressure also acts to consolidate layers of tape into a composite, and is shown schematically in Figure 1.10.
Figure 1.9. Optical micrograph of a PP fibre embedded in a PP matrix
(Figures 1.8 and 1.9 reproduced from Loos et al., 2001)

Figure 1.10. Schematic of consolidation of co-extruded tapes

Table 1.6 shows some mechanical properties of unidirectional composites produced using constrained co-extruded tapes compared to unidirectionally oriented PP composites reported in literature. As with the other composite systems, described previously, it is essential that fibre properties are retained in the final composite component, and so processing conditions are crucial. This retention is now simplified because the temperature processing window has now become much wider by combining constraining and co-extrusion coating of the tapes, and processing can occur at lower temperatures, thus reducing the risk of loss of fibre orientation.

These new developments using co-extruded PP tapes have been introduced previously (Schimanski, 2002) and shall be investigated further within this research. Standard composite materials feature two very different materials as fibre and matrix but this complicates recycling, which has become a focus of automotive industry following recent legislation. Thermoplastic single polymer composites can be manufactured which simplify recycling by requiring only melting and reprocessing. The mechanical properties of these composites depends strongly on the manufacturing route, and so far this has been very sensitive to deviation from optimum conditions.
Table 1.6. Manufacture of unidirectional oriented PP sheets by different production routes

<table>
<thead>
<tr>
<th>Method</th>
<th>Draw Ratio</th>
<th>$E_I$ [GPa]</th>
<th>$\sigma_I$ [MPa]</th>
<th>$E_{II}$ [GPa]</th>
<th>$\sigma_{II}$ [MPa]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roll-Drawn Billets</td>
<td>20</td>
<td>20</td>
<td>450</td>
<td>2</td>
<td>50</td>
<td>(Burke et al., 1987)</td>
</tr>
<tr>
<td>Drawn Sheets</td>
<td>14</td>
<td>7.5</td>
<td>250</td>
<td>-</td>
<td>-</td>
<td>(Lee and Schultz, 1985)</td>
</tr>
<tr>
<td>Hot Compacted PP Fibres</td>
<td>-</td>
<td>3.7</td>
<td>87</td>
<td>-</td>
<td>7</td>
<td>(Abo El-Maaty et al., 1996)</td>
</tr>
<tr>
<td>Co-extruded PP Tape (UD Composite)</td>
<td>17</td>
<td>13</td>
<td>385</td>
<td>1.5</td>
<td>4.5</td>
<td>(Alcock, this research)</td>
</tr>
</tbody>
</table>

1.7 Summary of this Research

The main objectives of this research are:

(i) The optimisation of interfacial and mechanical properties of co-extruded PP tapes for All-PP composites

(ii) The investigation of the processing parameters on the production of All-PP laminates, and the resulting mechanical properties

The first step is the creation of high modulus, high strength co-extruded PP tape. The factors affecting the mechanical properties are presented in Chapter 2, which also attempts to explain the effect of different tape drawing parameters using established models of microstructure of highly oriented polyolefins. The next step is to optimise the co-extrusion process to maximise the interfacial performance of All-PP composites. This is presented in Chapter 3, which investigates the effect of co-extrusion parameters on the interfacial properties of simple composites formed of bonded tapes and woven tape composites. Chapter 4 reviews the mechanical properties of unidirectional and woven fabric composites manufactured over a range of processing conditions to fully understand the processing window to produce thin composite plates. The dynamic properties of All-PP composites are then investigated in Chapter 5 to assess the temperature dependence and strain rate dependence on the tensile properties. Chapter 6 investigates the impact resistance of woven All-PP fabrics, by subjecting composite plates to penetrative and non-penetrative impact by falling weight tests and also ballistic testing to assess the performance against a range of possible impacts. With this understanding of mechanical properties obtained for All-PP plates, Chapter 7 reviews the range of processing parameters available to manufacture an All-PP component with a 3-dimensional geometry.

This publication is a partial reproduction of a PhD thesis by the same author (Alcock, 2004) written at Queen Mary, University of London, UK. The development of high modulus PP fibres and tapes has been the subject of a previous PhD thesis (Schimanski, 2002) within the same research project based at Technische Universiteit Eindhoven (TU/e), The Netherlands, and a parallel PhD thesis also performed at TU/e (Cabrera, 2004) investigates the production and processing of products from these All-PP composites.
Chapter 2

Drawing Semi-crystalline Polymers

2.1 Introduction

In the previous chapter, the various routes to reinforce PP were discussed, but since ease of recycling favours single polymer systems, this research will focus on the reinforcement of PP by orienting the molecules in the loading direction. However, it is important to understand the processes involved during drawing, in order to optimise the mechanical properties of the oriented polymer. When a semi-crystalline polymer such as a PP tape is deformed in the solid state, the deformation occurs through the reorientation of the crystalline regions and orientation and elongation of the amorphous regions. It has been shown that during tensile deformation of polypropylene, orientation occurred by a combination of orientation of the crystalline and amorphous phase at draw ratios $\lambda<9$, and above $\lambda=9$, orientation occurs solely due to the orientation and elongation of the amorphous regions (Yamada et al. 1981). Thus the high modulus of highly drawn ($\lambda>10$) PP is due to the orientation of the amorphous regions. These regions are referred to as tie molecules since they form bridges between highly crystalline lamellae. In a hypothetical, perfectly oriented semi-crystalline polymer, these tie molecules would be perfectly straight between crystal lamellae and so the modulus of the polymer fibre would be equal to the stiffness of the polymer molecule itself. These taut tie molecules explain the high stiffness seen in solid state drawn semi-crystalline polymers and are responsible for load transfer within the tape. Starting from a spherulitic structure, initial deformation first splits the spherulites into constituent lamella. It has proposed that the temperature of initial deformation becomes crucial to further drawability (McConkey et al. 1971). This expanded on a previous model (Hay and Keller 1965, 1966) which showed that when spherulites are deformed in tension, they fracture into individual lamellae connected by amorphous tie molecules. This is shown in Figure 2.1 (Samuels 1970).

When subjected to small deformations, the spherulite structure can deform elastically. As the yield stress of the polymer is exceeded, lamellae oriented parallel to the drawing direction become deformed plastically, resulting in the tilting of radial lamellae to become aligned perpendicularly to the drawing direction. Eventually, the spherulitic structure is lost as all the lamellae become parallel, normal to the drawing direction. The amorphous phase fills the volume between lamellae,
but has been excluded from this schematic for clarity. The drawing temperature is important because increased temperature allows greater rotation of the crystal lamellae from a radial orientation, as in the spherulite, to a transverse orientation in an elongated body with less crystal disruption.

Subsequent solid state drawing can be performed from the stacked lamellae model seen in Figure 2.1. Numerous reports have been published describing the morphological structure of solid state drawn semi-crystalline polymers, and this deformation process will be summarised here. The crystal lamellae are oriented as described above along the plane transverse to the drawing direction. These are linked together by tie molecules which constitute the amorphous phase of the polymer. With increasing draw ratio, these tie molecules orient along the direction of drawing and become taut and facilitate the transfer of load between the crystalline lamellae, both in the drawing process, and subsequent loading of fibre. The applied load on the lamellae shear them into smaller lamellae, still oriented transverse to the drawing direction, but now connected by taut tie molecules formed due to some unfolding of crystalline chains when lamellae shear.

This leads to the creation of microfibrils (crystalline regions consisting of columns of lamellae) linking larger lamellae together with bridges of oriented, taut tie molecules as represented in Figure 2.2. These microfibrils are considered to be composed of amorphous and crystalline regions loaded in series and since the taut tie molecules are also oriented, the whole structure possesses high stiffness in the longitudinal direction. During drawing at higher draw ratios, the large tension on the taut tie molecules can lead to some partial unfolding of folded molecules from the crystal lamellae to facilitate the creation of more tie molecules (Peterlin 1975). The formation of these microfibrils
leads a necking process; with the large extension in the drawing direction creating a negative pressure around the microfibrils by a Poisson contraction. This can be further explained by considering the Takayanagi model, which simulates a unit cell of a highly oriented semi-crystalline structure.

Figure 2.2. Schematic of the microfibrillar structure of a semi-crystalline polymer, with vertical orientation deformation reproduced from (Nagou and Azuma, 1979). C, C’, A and T represent perfect crystalline regions, defective crystalline regions, amorphous regions and taut tie molecules, respectively

Takayanagi et al, 1966, proposed a model to explain the separate mechanical contribution of amorphous and crystalline regions of such a structure during deformation. This is shown in Figure 2.3 and the tensile modulus of this structure is defined by equation 2.1. If the crystalline phase is seen as an incompressible structure then in order for the tensile deformation to occur, there must be an increase in $\varphi$, and a decrease in $\mu$. The decrease in $\mu$ is prevented by the incompressible lamellae width. This causes a negative pressure to build up in the transverse direction which leads to the creation of microvoids between the microfibrils (Peterlin 1971). Tapes or fibres which show this microvoiding are referred to as overdrawn.

$$
\frac{1}{E} = \frac{\varphi}{(1-\mu)E_c + \mu E_a} + \frac{1-\varphi}{E_c}
$$

2.1

Where

- $E$ = Tensile modulus of structure
- $E_c$ = Tensile modulus of crystalline phase
- $E_a$ = Tensile modulus of amorphous phase

These microvoids can be clearly seen in the SEM image shown in Figure 2.4. The transition from dense to microvoided polymer has been subsequently identified in numerous drawn polymer systems including die drawn polypropylene rods (Coates and Ward 1979), drawn polypropylene fibres (Abo El-Maaty et al. 1996) and has been witnessed in other polymers such as polyethylene

The production of overdrawn tapes is uncommon in industry. The onset of overdrawing is considered a limiting factor in the manufacture of highly drawn polymer fibres, since it is associated with increased fibre breakage in production. However, such a decrease in stability was not seen in this research and so a maximum drawability was sought to achieve greatest molecular orientation and hence largest mechanical properties. Although the relationship between draw ratio and tensile strength is subsequently seen to be non-linear, with only a small increase in tensile strength above $\lambda=10$, the tensile modulus of the tapes continues to increase with draw ratio during overdrawing, and this increased modulus is required in order for All-PP tapes to compete with glass fibres as composite reinforcements. The overdrawing (microvoiding) does not occur in a single area, but as many smaller voids parallel to the drawing direction of the tape.

Table 2.1 shows a comparison of mechanical properties of oriented PP produced via gel spinning and solid state drawing production routes. Even though mechanical properties of gel spun PP exceed that of solid state drawn PP, the gel spinning route is made less cost effective due to the need for solvents and subsequent solvent recovery, and is problematic due to long crystallisation times of PP. Ultra high molecular weight polypropylenes are also more expensive than lower molecular weight polypropylenes, and in order to create a competitive finished product, these costs are crucial to the feasibility of the material. In addition to the choice of orientation route, it is also beneficial to produce tapes, as opposed to fibres. In the drawing process, tape geometries are more stable, and also due to lower volume to surface area ratios, experience more uniform heating in the drawing ovens. With these considerations in mind and the advantages in close packing in subsequent consolidation processes, this research is based on solid state deformation of melt spun PP tapes.
2.2 Experimental Procedure

2.2.1 Drawing Polypropylene Tapes

The PP tapes manufactured are co-extruded with a copolymer layer, with a A:B:A structure (A refers to copolymer, B refers to homopolymer) of approximate proportions of 5.5%:89%:5.5%. For the interest of this chapter, the presence of this thin copolymer layer will be ignored unless specifically mentioned.

The tape production line used for the creation of these tapes, shown schematically in Figure 2.5, is modelled on an industrial production line, the use of which is kindly provided by Lankhorst Indutech.
BV, Netherlands. Two single screw extruders are employed to extrude homopolymer and copolymer, respectively, into a heated co-extrusion (coat-hanger) manifold. In the manifold, the layers are combined and are extruded through a thin extruder nozzle measuring ~10cm wide. The extrudate is quenched by winding on a cold drum, rotating at 6\text{m.min}^{-1}, submerged in a cold water bath, and then proceeds to the first of two drawing ovens. In the first drawing oven, the tape is drawn to $\lambda_i=6$, and exits the oven at ~36\text{m.min}^{-1}.

![Diagram of co-extrusion and solid state drawing production line](image)

**Figure 2.5. Schematic of co-extrusion and solid state drawing production line**

The tape is then directly drawn in a second oven, in which the second draw ratio, $\lambda_{ii}$, is achieved. The multiple of the first draw ratio, $\lambda_i$, and the second draw ratio, $\lambda_{ii}$, gives total draw ratio, $\lambda$:

$$\lambda = \lambda_i \times \lambda_{ii}$$  \hspace{1cm} (2.2)

The first oven temperature and initial draw ratio have been optimised by previous studies performed using this equipment (Schimanski 2002). The second drawing conditions have been varied for the investigations of this chapter, but default settings are described in Table 2.2. Due to extrusion, it is likely that some orientation is already present in the tapes before drawing, but this is ignored in this study since the reported draw ratios are merely comparative. After exiting the second oven, the tape is collected by winding onto a bobbin.

**Table 2.2. Default co-extrusion parameters (To give $\lambda=15$)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>From Extruder</th>
<th>Oven 1</th>
<th>Oven 2</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape Speed</td>
<td>6 m.min$^{-1}$</td>
<td>36 m.min$^{-1}$</td>
<td>90 m.min$^{-1}$</td>
<td>90 m.min$^{-1}$</td>
</tr>
<tr>
<td>Tape Temperature</td>
<td>20$^\circ$C</td>
<td>60$^\circ$C</td>
<td>160$^\circ$C</td>
<td>-</td>
</tr>
<tr>
<td>Draw Ratio</td>
<td>1</td>
<td>$\lambda_i = 6$</td>
<td>$\lambda_{ii} = 2.5$</td>
<td>$\lambda = 15$</td>
</tr>
</tbody>
</table>
The ratio of homopolymer to copolymer can be controlled by adjusting the output of each extruder. Since the thickness of the copolymer layer is very low, the copolymer is extruded from a smaller diameter extruder than the homopolymer. Prior to tape manufacture, the output of the extruders was determined as a function of the relative screw speed of the two extruders, and this is used to calculate relative proportions. This calculation was verified by measuring the thickness of undrawn tapes with varying proportions and comparing with predicted values. In these measurements, die swell of the co-extrudate is ignored since a proportional swell of homopolymer and copolymer is assumed. The choice of molecular weight ($M_w$) PP used is important, since very large molecular weights limit solid state drawability and ultimately affect mechanical properties. However, in this research the choice is governed by the necessity to match viscosity ($\eta$) of the homopolymer with that of the copolymer. To achieve layer stability during co-extrusion, the viscosity of the two polymer grades used must be similar (Dooley 2002). Dissimilar viscosities lead to displacement of the low viscosity melt by the high viscosity melt immediately after co-extrusion, as illustrated in Figure 2.6. Although, this schematic exaggerates the effect witnessed during co-extrusion, even a small viscosity mismatch led to an uneven tape surface, and a characteristic ‘shark-skin’ finish is seen on the tape. These surface irregularities lead to stress concentrations and premature fracture in drawing, limiting the maximum attainable draw ratio.

![Figure 2.6. The effect of viscosity mismatch in co-extruded A:B:A tapes

(i) $\eta_A < \eta_B$, (ii) $\eta_A = \eta_B$, (iii) $\eta_A > \eta_B$](image)

2.2.2 Rheological Measurements

Rheological analysis of several grades of polypropylene was performed using a rheometer equipped with cone and plate fittings (Rheometric Scientific, USA). Cone and plate rheometry was chosen because the geometry of the cone on the upper surface of the rheometer gives a homogenous shear.
strain across the radius of the specimen, and is a respected method to measure large variations in viscosity (Macosko 1994). A schematic of the cone and plate set-up is shown Figure 2.7. The lower plate is stationary and the upper cone oscillates; this rotation is transmitted through the polymer melt and a response is measured as a torque on the lower plate.

![Schematic of cone-plate rheometry apparatus](image)

**Figure 2.7. Schematic of cone-plate rheometry apparatus**

The moment, \( M \), provides a measurement for shear stress, \( \tau \), described in equation 2.3.

\[
\tau = \frac{3M}{2\pi R^3}
\]

Where

- \( R \) = Radius of plate

The shear stress, \( \tau \), is sinusoidally oscillating, and so it can be broken down into two waves of the same frequency: an elastic component with in-phase with \( \tau \), and a viscous component 90° out of phase with \( \tau \).

\[
\tau = \tau' + \tau'' = \tau'_0 \sin \omega t + \tau''_0 \cos \omega t
\]

Where

- \( \tau' \) = Elastic component of shear stress
- \( \tau'' \) = Viscous component of shear stress
- \( \omega \) = Angular velocity vector
- \( t \) = Time
The shear strain rate $\dot{\gamma}$, is defined as:

$$\dot{\gamma} = \frac{\Omega}{\beta}$$  \hspace{1cm} (2.5)

Where $\Omega$ = Angular velocity
$\beta$ = Angle between cone slope and plate

From shear strain rate and shear stress, the viscosity, $\eta$, can be calculated.

$$\eta = \frac{\tau}{\dot{\gamma}}$$  \hspace{1cm} (2.6)

But, to consider the elastic and viscous components of viscosity, $\eta'$ and $\eta''$, respectively,

$$\eta' = \frac{\tau'}{\dot{\gamma}_0}$$  \hspace{1cm} (2.7)

$$\eta'' = \frac{\tau''}{\dot{\gamma}_0}$$  \hspace{1cm} (2.8)

The measured complex viscosity, $|\eta^*|$, is defined as a complex number with $\eta'$ and $\eta''$ as real and imaginary parts, respectively.

$$|\eta^*| = \sqrt{\eta'^2 + \eta''^2}$$  \hspace{1cm} (2.9)

Thus the complex viscosity of a polymer melt at 220°C was determined. Since polymer melts exhibit non-Newtonian behaviour, the relationship between $\dot{\gamma}$ and $|\eta^*|$ is non-linear, and at very low shear strain rates, a maximum value of $|\eta^*|$ is reached. This maximum, $|\eta_0^*|$, is termed the zero shear viscosity and will be used in this chapter to compare polymer melts. Viscosity measurements are further supported by melt flow indexing (MFI) of the polymer grades investigated. MFI tests were performed according to ASTM D1238, using a Davenport (UK) melt flow indexer. Experiments were performed at 230°C, using a 2.16kg mass to extrude the melt through a 2mm diameter die. The mass extruded was weighed after 5 minutes flow using a balance accurate to ±1mg.

### 2.2.3 Density Measurements

The density of polypropylene tapes, $\rho$, was determined by applying the Archimedes principle, which states that a body submerged in a fluid will experience an up-thrust equal to the weight of the fluid dispersed. Practically, the apparent mass of a specimen is measured in air and in a liquid (water); the ratio of the apparent mass in air to the difference between the apparent mass in air and in liquid is equal to the ratio of the density of the liquid to the density of the specimen.
This can be described algebraically as:

\[ \rho = \rho' \left( \frac{m'}{m' - m''} \right) - a' \]

Where,
- \( \rho \) = Density of sample
- \( \rho' \) = Density of liquid
- \( a' \) = Buoyancy effect due to air (\( a = 0.001 \text{g.cm}^{-3} \))
- \( m' \) = Apparent mass measured in air
- \( m'' \) = Apparent mass measured in liquid

The equipment used is shown schematically in Figure 2.8. The specimen is measured in accordance with ASTM D3800, firstly by measuring apparent mass of the specimen in air by placing it in a sample pan which is connected to a measuring frame linked to a microbalance. The water is kept in a container, raised above the microbalance by a bridge. In this way, the up-thrust of the submerged specimen can then be measured in the lower sample pan, without any measurement of the mass of the specimen or the fluid. The density of the water was determined by using a calibrated 10ml glass volume, and the temperature of the water was kept constant during testing to eliminate any fluctuation in water density.

2.2.4 Tensile Testing of Tapes

Tensile tests to failure of single polypropylene tapes were performed using a Hounsfield tensile testing machine equipped with a 1kN load cell, special force reducing fibre clamps and QMat data acquisition software. A crosshead displacement of 5mm.min\(^{-1}\) and a gauge length of 200mm were used. Strength is defined here as the maximum stress recorded in tensile failure, and the strain to failure is defined here as the strain at which this load occurred. Typical loads to failure of the tape are in the region of 75N - 200N, depending on tape dimensions. Since the cross sectional area of the tapes decreases with increasing draw ratio, specimen dimensions vary, but are in the region of 2-4mm wide and 0.06-0.15mm thick.

Tensile tests to determine tensile modulus were performed using an Instron Tensile testing machine equipped with a 1 kN load cell, standard grips and Merlin data acquisition software. A crosshead displacement of 64mm.min\(^{-1}\) and a gauge length of 640mm were used (approximate strain rate of 0.1min\(^{-1}\)). Preliminary comparisons between this method and an alternative method using a self supported extensometer yielded equal moduli within the range of experimental scatter. Modulus of each specimen is calculated as the gradient of the stress vs. strain curve between 0.1% and 0.4% strain, which is seen to be linear for these tapes. The values presented subsequently for moduli, strength and strain to failure are the average of at least 5 repetitions of each test.
2.2.5 Trouser Tear Testing of Tapes

In addition to tests to determine the properties of the tape in longitudinal direction, trouser tear tests were performed to obtain information on tape anisotropy. The tests were performed using a Hounsfield tensile testing machine, fitted with a 5N load cell, specially developed low mass clamps and QMat data acquisition software. A crosshead displacement of 250mm.min\(^{-1}\) and a specimen of 500mm length was used. A pre-crack is introduced to the edge of a tape with a razor blade, and each side of the split tape is placed in opposing grips of the tensile machine. The displacement of the grips forces the crack to propagate along the tape length; since the polymer molecules within the tape are oriented in the tape direction, the crack easily propagates along the tape length and does not readily deviate to the edges of the tape. The test specimen is shown schematically in Figure 2.9.

The force of crack propagation, \(F\), quickly reaches a constant value, and this gives a value for fracture surface energy, \(G_C\), as described by equation 2.11 (Anderton and Treloar 1971).

\[
G_C = \frac{2F}{t'}
\]

2.11

Where 
- \(F\) = Tear force 
- \(t'\) = Tape thickness

Tensile deformation of the arms of the sample is ignored due to the low forces involved in tearing the sample and the high stiffness of the tapes. As before, the data reported later in this chapter are averages based on at least 5 repetitions.
2.2.6 Free Shrinkage Measurements

Since the compaction process requires the heating of tapes, it is crucial to determine how the tapes behave at elevated temperatures. The polymer molecules have been highly oriented by drawing, and upon heating there will be significant relaxation and a decrease in mechanical properties. To assess the ‘free’ shrinkage of polypropylene tapes, i.e. shrinkage during exposure to elevated temperatures with no external pressure applied, sets of 5, 1m lengths of tapes were hung in a preheated, circulating air oven controlled by an internal thermostat and monitored by an independent thermometer fitted with two PT100 temperature probes placed at different locations in the oven. The air temperature was constant, and uniform (±1°C) within the oven. Preliminary tests showed that for all temperatures, shrinkage as a function of duration in the oven increases logarithmically with time (see Figure 2.10). Total shrinkage is defined as fraction of initial sample length remaining after exposure to elevated temperature. Considering this, all free shrinkage measurements were performed by placing tapes in an oven, allowing the oven to return to required temperature following opening the oven door, and then holding for 25 minutes (total duration in oven is approximately 30 minutes). Figure 2.10 suggests that around 80% of total possible free shrinkage has occurred for each tape after this time.

2.2.7 Shrinkage Force Measurement of Tapes

It is also important to understand how much force is exerted by a tape as it these relaxation processes occur. Shrinkage force measurements were determined by placing 30cm lengths of tape between opposing grips of an Instron tensile testing machine fitted with a 1kN load cell, and a circulating air oven controlled by an internal thermostat. Temperature was also measured, as before, using a thermometer with two PT100 temperature probes monitoring air temperature at two locations within the oven. The circulating air showed good thermal uniformity within the oven. The test set-up is shown schematically in Figure 2.11. The specimen is placed inside the oven and the oven temperature is raised from room temperature until failure of the tape (typically ~190°C) at a rate of approximately 10°C.min⁻¹.
No displacement of the crosshead was applied; a force due to the shrinkage of the tape was recorded with increasing temperature on a data acquisition computer running Merlin software. Prior to testing, grips were heated to reduce thermal expansion of grips during testing and so limiting this affect on shrinkage force measurements. A preload of 1N (~7MPa) was applied to the tapes before heating to assure a taut specimen necessary to accurately measure shrinkage force. 5 repetitions of each tape were tested to provide an average value for the shrinkage force of each tape.
2.3 Results and Discussion

2.3.1 Rheological Analysis

In order to match viscosity to provide a stable co-extruded tape, cone-plate rheology was performed as described earlier, for 7 polypropylene homopolymers and 4 random block propylene-ethylene copolymers in a molecular weight range suitable for extrusion and fibre drawing (see Table 2.3).

Table 2.3. Suppliers of the PP grades used

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>Polymer Type</th>
<th>Manufacturer</th>
<th>MFI [g.10min⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Random block PP/PE copolymer</td>
<td>Basell</td>
<td>3.5</td>
</tr>
<tr>
<td>C2</td>
<td>Random block PP/PE copolymer</td>
<td>Basell</td>
<td>5.5</td>
</tr>
<tr>
<td>C3</td>
<td>Random block PP/PE copolymer</td>
<td>DSM</td>
<td>8</td>
</tr>
<tr>
<td>C4</td>
<td>Random block PP/PE copolymer</td>
<td>DSM</td>
<td>40</td>
</tr>
<tr>
<td>H1</td>
<td>PP homopolymer</td>
<td>DSM</td>
<td>0.3</td>
</tr>
<tr>
<td>H2</td>
<td>PP homopolymer</td>
<td>DSM</td>
<td>0.8</td>
</tr>
<tr>
<td>H3</td>
<td>PP homopolymer</td>
<td>Basell</td>
<td>1</td>
</tr>
<tr>
<td>H4</td>
<td>PP homopolymer</td>
<td>Basell</td>
<td>3</td>
</tr>
<tr>
<td>H5</td>
<td>PP homopolymer</td>
<td>DSM</td>
<td>13</td>
</tr>
<tr>
<td>H6</td>
<td>PP homopolymer</td>
<td>DSM</td>
<td>25</td>
</tr>
<tr>
<td>H7</td>
<td>PP homopolymer</td>
<td>DSM</td>
<td>47</td>
</tr>
</tbody>
</table>

Polymer melts behave in a non-Newtonian fashion, i.e. viscosity and shear rate are non-linear. This is seen in Figure 2.12, which shows the relationship between shear rate (frequency) and complex shear viscosity. With decreasing frequency, complex shear viscosity reaches a plateau value due to a shear thinning effect. This plateau value is the maximum complex shear viscosity, and is termed the zero shear viscosity. These results show a wide range of shear rates, but the relevant shear rates for co-extrusion vary within the range 1 – 100 s⁻¹ (Macosko 1994). Figure 2.13 shows the relationship between the zero shear viscosity and MFI for all the polymer grades considered. It is clear that while no exactly matching viscosities were found from the range of polymers considered, the blend of two similar homopolymers: H4 and H5 (Basell, and DSM, both Netherlands) would match the viscosity of one of the copolymers: C2 (Basell, Netherlands). These three polymer grades are presented in Table 2.4.

Table 2.4. Polymer grades chosen for this research

<table>
<thead>
<tr>
<th>Product</th>
<th>Polymer Type</th>
<th>$M_n$ [kg.mol⁻¹]</th>
<th>$M_n/M_n$ [-]</th>
<th>MFI [g.10min⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4</td>
<td>PP homopolymer</td>
<td>350</td>
<td>5.6</td>
<td>3</td>
</tr>
<tr>
<td>H5</td>
<td>PP homopolymer</td>
<td>280</td>
<td>5.8</td>
<td>13</td>
</tr>
<tr>
<td>C2</td>
<td>PP/PE random copolymer</td>
<td>320</td>
<td>4.3</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Subsequently, all tapes were manufactured using a 1:1 weight ratio mix of H4 and H5 (this blend is hereafter termed the ‘homopolymer’) as the ‘B’ layer, and C2 (hereafter termed the ‘copolymer’) as the ‘A’ layer.

![Complex shear viscosity data from cone-plate rheology](image1)

**Figure 2.12** Complex shear viscosity data from cone-plate rheology

![Zero rate shear viscosity vs. melt flow index](image2)

**Figure 2.13.** Zero rate shear viscosity vs. melt flow index
2.3.2 Draw Ratio Dependant Properties

Having established the best suited materials for co-extruded tape production, tapes were produced with a range of draw ratios, $\lambda$, to determine the effect of draw ratio on the mechanical properties of the tapes. With increasing draw ratio there is a noticeable change in appearance of tapes at a draw ratio of $\lambda=9$; below this draw ratio, the tapes appear transparent, but above this draw ratio they are opaque. This is shown in Figure 2.14, for a range of tapes with increasing draw ratio. The opacity is first seen in the centre of the tape, but with increasing draw ratio, eventually covers the entire tape. This phenomenon is due to a transition from a microvoided to a highly micro-fibrous structure, established during drawing as described previously (see section 2.1.2). There is lower reduction in the exterior dimensions of the tape during drawing, since microvoiding relieves transverse Poisson contractions, but these voids lead to a reduction in total density of the tape. Similar voids have been reported on the surface of drawn polypropylene films (Olley and Bassett 1994). These were attributed to a large crystal morphology, present in the undrawn film, which provides regular defects assisting the initiation of microvoids with increasing draw ratio.

![Figure 2.14. Photograph of tapes drawn at increasing draw ratios](image)

Tapes with varying draw ratio were produced and the tape density was measured using the Archimedes principle detailed in section 2.2.2 to quantify this effect. Figure 2.15 shows a graph of the measured tape density with increasing draw ratio. It is clear that density is approximately constant with increasing draw ratio until $\lambda=9$, above which density rapidly drops. This decrease is associated with the change in transparency of the tape, and is due to microvoiding within the tape (Abo El-Maaty et al. 1999; Schimanski 2002). At $\lambda=17$, density has reached 0.73g.cm$^{-3}$, and so density has been reduced by almost 20%.

Such a decrease in density can either be attributed to a uniform decrease in the density of the polymer by 20%, which is impossible since the density of crystalline PP is only 10% higher than the density of amorphous PP ($\rho_{\text{CrystallinePP}} \approx 0.94\text{g.cm}^{-3}$ and $\rho_{\text{AmorphousPP}} \approx 0.85\text{g.cm}^{-3}$). Therefore such a large decrease in density can only be attributed to the presence of voids within the tape. This
decrease in density can be seen as positive for the development of these tapes as an engineering material, but first any possible negative aspects of these voids must be established.

The tensile strength and strain to failure of these tapes is shown in Figure 2.16. Like density, the strength and strain to failure as a function of draw ratio is also non-linear. Increasing draw ratio leads to a large decrease in strain to failure from \(>300\%\) for undrawn polypropylene to around 7\% for \(\lambda=17\). As would be expected, tensile strength also increases with increasing draw ratio, but is clearly less dependent on draw ratio. A similar behaviour has been reported for acetyl fibres (Clark and Scott 1974). At \(\lambda<9\), strength increases, but at \(\lambda>9\), strength becomes more constant, only showing a real increase at \(\lambda>14\). This is has been explained by Yamada et al., who showed that initial drawing is due to orientation of crystalline regions and amorphous regions, while drawing above \(\lambda=10\) is mainly due to increasing orientation of the amorphous phase between crystals (Yamada et al. 1981). Since tensile strength is mainly governed by crystal orientation (Flood and Nulf 1990), it is reasonable to assume little further increase in tensile strength with increasing draw ratio above \(\lambda=10\). Thus is in the production of ropes, where strength is critical, a draw ratio of 10 is sufficient. Any increase in tensile strength will also be opposed by the formation of weak void-rich areas, possibly leading to stress concentrations and failure of the tape. Figure 2.16 shows that this is the draw ratio in which major voiding starts to form, so this is a likely explanation.

Also shown on Figure 2.16 is the specific tensile strength. Since density decreases with increasing draw ratio, measuring the cross sectional area of the tape is no longer a valid method to determine stress within the tape. The specific strength takes into account the reduction in cross sectional area, but cannot account for any stress concentrations that microvoiding may cause. Similarly, Figure 2.17 shows the tensile modulus of the same group of tapes. Since the modulus is measured at low strains, the presence of micro-voids will not alter the modulus except by reducing the average cross sectional area of the tape.
As would be expected, as $\lambda$ increases, modulus increases, reaching a modulus of 15GPa at $\lambda=17$. Again, the specific modulus shows a greater increase since the density decreases with increasing draw ratio accounting for the presence of microvoids. However, the specific modulus of the tape exceeds 20GPa.g$^{-1}$.cm$^3$ which compares very well to the maximum reported modulus (19GPa) of a solid state oriented PP sheet (Burke et al. 1987). Since this sheet is roller drawn, the formation of microvoids is prevented by the transverse pressure applied by the rollers, and so the density of the sheet equals that of bulk PP (~0.91 g.cm$^{-3}$). Thus the specific modulus obtained by Burke et al., approaches 21GPa.g$^{-1}$.cm$^3$, very close to the specific modulus seen here.
With increasing orientation of the polymer it would be expected that the transverse properties of the tape would decrease. Figure 2.18 shows the fracture surface energy (tear resistance) of the same group of tapes with increasing draw ratio, compared to values previously reported for oriented PP in literature (Sims 1975; Mahajan et al. 1996). As draw ratio increases, data from Sims shows a large decrease in fracture surface energy with increasing draw ratio. The experiments performed for this thesis show no real decrease in tear resistance with increasing draw ratio although values are within the same range as those published by Sims and also by Mahajan et al. Sims suggests that the decrease in tear resistance with increasing orientation is not due to increased molecular alignment, but a decrease in plasticity in the vicinity of the crack that reduces the energy absorbed in crack propagation. Considering this assumption, the greater tear resistance of the co-extruded tapes in this thesis may be attributable to the unoriented copolymer layer on either surface of the tape providing some plasticity and hence a greater energy absorption. This higher resistance to plastic deformation would lead to a greater energy consumption by tearing and hence a higher tear resistance value. From these tape tearing results, if there is a negative influence on transverse properties of the tape due to high degree of orientation, it appears to be compensated by the presence of the tough copolymer layer.

![Figure 2.18. Fracture surface energy (tear resistance) vs. draw ratio](image)

2.3.3 Draw Temperature Dependant Properties

The co-extruded tapes are drawn in a two stage drawing process. The first drawing stage provides some initial orientation, but ultimate drawing is performed in the second stage. This initial orientation is necessary to allow drawing at higher temperatures in the second drawing stage. In this second drawing stage, the drawing temperature can have a dramatic effect on mechanical and interfacial properties (see Chapter 3). A fundamental investigation into the effect of drawing temperatures can be found in a previous publication (Schimanski 2002). The tapes described in the previous section were subject to a second oven drawing temperature of 160°C. For the next group of tests, tapes were produced at a constant $\lambda=13$ and increasing drawing temperature in the second oven.
from 160°C to 190°C; drawing above 190°C was impossible due to tape breakage, since this is the melting temperature of a constrained fibre (see Figure 1.19). The first observation made from increasing drawing temperature is a return to a transparent tape appearance. Figure 2.19 shows the appearance of 4 tapes with increasing drawing temperature from 160°C to 190°C in 10°C increments. This leads to the direct assumption that since this opacity is caused by micro-voids in the highly oriented homopolymer, these must have either closed or been prevented from forming during drawing at elevated temperatures.

![Figure 2.19. Photograph of tapes drawn at increasing drawing temperatures](image)

**Figure 2.19.** Photograph of tapes drawn at increasing drawing temperatures

Figure 2.20 shows the variation in density of the tapes as a function of the second oven drawing temperature. It is clear that density increases with drawing temperature, reaching the density of bulk PP at 190°C. The increase in density seems to be approximately linear, and appears to be due entirely to the decreasing proportion of voids in the tape, since the density of bulk polypropylene is
reached in high draw temperature tapes. Clearly, upon increasing drawing temperature, the reduced viscosity of PP leads to drawing occurring in a melt rather than a solid state.

Figure 2.21. Tensile strength, specific tensile strength and strain to failure vs. drawing temperature

Figure 2.21 shows the effect of drawing temperature on the strength and strain to failure of the tapes. There is very little change in the values recorded despite the change in density and the removal of the micro-voids. There is a small increase in the strength of the tapes drawn at 190°C, possible due to the closure of these voids leading to a reduction of stress concentrations. Since this is the only increase in strength seen despite an almost linear increase in density, it is likely that the longitudinal voids are closing or becoming smaller but are still structural weak points. The tensile moduli of these tapes are shown in Figure 2.22 as a function of the second oven drawing temperature. This graph shows that there is a gradual decrease in tensile modulus with increasing drawing temperature. The effect is even more obvious when the specific properties are considered. Increasing the drawing temperature from 160°C to 190°C results in a decrease in modulus of approximately 15%.

The increase in second oven drawing temperature can be considered as the opposite of an increase in the draw ratio, with a reduction in tensile modulus and a return to the transparent, high density tape. When drawing at a higher temperature it is likely that higher levels of molecular mobility allow some relaxation (hence the reduction in modulus) while drawing, and as temperature is increased, eventually this reaches a point where relaxation is great enough to allow tape failure. This molecular mobility can also explain the absence of voids at higher drawing temperatures; since voids occur due to local necking within the tape, an increase in temperature discourages necking by encouraging flow and deformation of amorphous regions into low pressure areas and so promotes a more uniform deformation (Peterlin 1978). It is clear that increasing the drawing temperature can be used as a method to produce transparent tapes with a small penalty in tensile modulus, and no loss of tensile strength. An exciting development for further research could be the development of transparent All-PP composites from these transparent tapes.
2.3.4 Free Shrinkage of Tapes

Ultimately, the tapes described in this research are being produced as a structural reinforcement element for All-PP composites. A wide range of processing routes can be considered, but all feature heating of the tape to facilitate consolidation. In addition to composite fabrication, thermal stability of the tapes is also desirable for elevated temperature exposure of the final composite part in use to prevent loss of mechanical properties and warpage.

The most direct measurement of shrinkage is the ‘free shrinkage’. For the clarity of this section, heating applied to cause shrinkage of the tapes will be quantified as “shrinkage temperature”, while temperature used in drawing the tapes will be referred to as “drawing temperature”. Figure 2.23 shows the degree of shrinkage after exposure to various oven temperatures of tapes with increasing draw ratio. Shrinkage is clearly non-linear, increasing with increasing oven temperature, but from this Figure, the relationship between shrinkage and draw ratio is ambiguous. Figure 2.24 represents the same series of data, but with the shrinkage shown as a function of draw ratio, for various discrete oven temperatures. From this graph, it is clear that there is an increase in free shrinkage for λ<9 with increasing draw ratio.

This is predictable since the applied temperature encourages relaxation and molecular reorganisation. However, as λ>9, there is a decrease in free shrinkage of the tape, with shrinkage at λ=14 being equivalent to shrinkage at λ=5. This is explained by considering the increasing alignment of tie molecules with increasing draw ratio. Yamada et al. showed that when drawing PP to λ≤9, orientation occurred by a combination of alignment of the crystalline lamellae and amorphous regions. When drawing above this, orientation mainly occurred by alignment of the amorphous regions, with the formation of many taut tie molecules (Yamada et al. 1981). The mechanism of thermal shrinkage is via loosening of these taut tie molecules, reverting to an unaligned state and thus pulling the lamellae closer together. There is an increase in the volume
fraction of taut tie molecules with increasing draw ratio (Taraiya et al. 1988), but these also become more thermally stable due to their increased alignment. Groups of parallel taut tie molecules become highly oriented, tightly packed and can be considered to be analogous to crystalline units, and thus have increased thermal stability compared to amorphous molecules (Ward 1984). This has been modelled by Pakula and Trznadel, who describe highly oriented taut tie molecules as being frozen in position and require greater heat to initiate shrinkage than less ordered molecules (Trznadel et al. 1985; Pakula and Trznadel 1985).

![Figure 2.23. Free shrinkage vs. shrinkage temperature](image1)

**Figure 2.23. Free shrinkage vs. shrinkage temperature**

![Figure 2.24. Free shrinkage vs. draw ratio](image2)

**Figure 2.24. Free shrinkage vs. draw ratio**
The relationship between drawing temperature and shrinkage is less complex and is shown in Figure 2.25. The general trend is similar to that seen in Figure 2.23; shrinkage increases with shrinkage temperature. Figure 2.26 represents the same data, with shrinkage plotted as a function of drawing temperature for a range of discrete shrinkage temperatures. There is an increase in thermal stability with increasing drawing temperature. At higher drawing temperature, some relaxation is possible during drawing, reducing the amount of residual strain locked in the microstructure of the tapes. As described previously, an increase in drawing temperature leads to greater chain mobility, and so a more relaxed microstructure.

**Figure 2.25.** Free shrinkage vs. shrinkage temperature

**Figure 2.26.** Free shrinkage vs. drawing temperature
Since both the tensile modulus and the free shrinkage of highly oriented PP are controlled by tie molecules in the amorphous phase, the mechanical properties following shrinkage were investigated. Figure 2.27 shows the residual tensile modulus following free shrinkage of tapes initially drawn to $\lambda=17$. The tensile modulus decreases with increasing shrinkage since the shrinkage is caused by relaxation of the taut tie molecules which facilitate stress transfer through the tape. The loss in tensile modulus with shrinkage is quite dramatic; a shrinkage of just 14.5% length results in a 73% loss of modulus.

![Figure 2.27. Residual tensile modulus following shrinkage](image)

This shrinkage is equivalent in length to returning from a draw ratio, $\lambda=17$ to $\lambda\approx14$, but equivalent in modulus to returning to $\lambda\approx6$. Thus thermal shrinkage is not the complete reversal of solid state drawing, and draw ratio and tensile modulus are not directly linked, as could be assumed from Figure 2.17. The sudden loss in tensile modulus seen at very low shrinkage ($\sim1\%$ length) is due to the relaxation of taut tie molecules. It is conceivable that as soon as these relax, load transfer between crystalline regions is reduced. During the heating of the tape to allow free shrinkage, it is also possible that small slippage in crystalline regions may allow taut tie molecules to relax (Boyd 1985), as shown in Figure 2.28. The drop in tensile modulus while tensile strength remains constant reinforces the theory that modulus is controlled by alignment of tie molecules, where as the strength is controlled by crystal orientation and structural effects such as microvoiding (Flood and Nulf 1990).

This would allow relaxation and decrease in tensile modulus without an obvious macroscopic shrinkage. The sudden loss in modulus was not reported in PP tapes with a much lower draw ratio (Le Bozec et al. 2000) since there are very much fewer taut tie molecules present in such a structure. These free shrinkage experiments illustrate the effect of microstructural changes on the macrostructure of the tape, and give good indications of the processes involved.
2.3.5 Shrinkage Force of Tapes at Elevated Temperatures

The shrinkage force has been investigated to further clarify the effect of heating a highly oriented PP tape. During heating of a PP tape constrained by fixed ends, shrinkage is prevented, but the same mechanisms that cause shrinkage cause a retractive stress to be experienced by the tape constraints. Figure 2.29 shows the magnitude of the maximum shrinkage stresses as a function of draw ratio. As draw ratio increases to $\lambda \approx 12$, shrinkage force increases, but decreases as $\lambda > 12$. The volume fraction of taut tie molecules increases with draw ratio, so the trend of the maximum shrinkage force cannot be solely due to changing volume fractions of taut tie molecules. Since shrinkage forces would be expected to increase together with draw ratio, these results reinforce the idea that as draw ratio increases, these taut tie molecules become arranged in a crystalline morphology and so possess greater thermal stability. Therefore, the decrease in maximum shrinkage stress must be due to a
combination of increasing shrinkage stress of ‘active’ retracting taut tie molecules, and a decrease in the volume fraction of taut tie molecules retracting. The magnitude of these shrinkage forces is similar to that reported in literature (De Candia et al. 1985) although since the maximum draw ratio considered by De Candia et al. was \( \lambda = 11 \), a reduction in shrinkage stress at higher draw ratios was not reported.

Figure 2.30. Shrinkage stress vs. shrinkage temperature following annealing at a range of temperatures

This decrease in shrinkage stress is not seen in high moduli gel spun UHMW-PP fibres (Bastiaansen and Lemstra 1989) which show a maximum shrinkage force of \(~60\text{MPa}\), and a tensile modulus of 35GPa. In this particular case, it would appear that gel-spun PP fibres are not as thermally stable as solid state drawn PP fibres, but still possess much higher moduli due to the higher achievable draw ratios. Figure 2.30 shows typical curves of shrinkage stress as a function of increasing temperature, during heating. As temperature increases, shrinkage stress increases as molecular movement encourages relaxation and reordering. The shrinkage stress passes through a maximum and then as the tape begins to melt, stress transfer along the tape length is lost and the perceived shrinkage stress decreases and ultimately leads to tape failure when the tape yields and breaks. The aims of this investigation are to understand and so control the thermal shrinkage of these PP tapes. Since free shrinkage (see Figure 2.27) shows a sudden decrease in tensile moduli with a very small shrinkage, it is possible that this immediate relaxation may be beneficial to the stability of the tapes. Figure 2.30 shows the effect of free annealing on the shrinkage stress behaviour of PP tapes with \( \lambda = 17 \) after being annealed in an oven at various temperatures for 20 minutes. The unannealed tape exerts a shrinkage stress at 40\(^\circ\)C and shows the greatest shrinkage stress throughout. For the tapes which have been annealed, two important changes in behaviour can be observed. Firstly, with increasing annealing temperature the maximum shrinkage stress decreases, dropping to almost half the shrinkage stress of the unannealed tape, shown in Figure 2.31. Secondly, the onset of shrinkage is seen to decrease with increasing annealing temperature. Tapes annealed at 140\(^\circ\)C, do not show a substantial shrinkage force until they are heated to 120\(^\circ\)C. By free
annealing highly oriented PP tapes, the thermal stability is improved by both a decrease in shrinkage stress, and an increase in temperature of the onset of shrinkage. This has been reported previously (Flood and Nulf 1990), and an annealing stage may be considered as an integral addition to the creation of future PP tapes. During the free annealing process taut tie molecules will relax and cause shrinkage in the tape due to the mechanisms described previously and so a loss of modulus can be expected. This loss in modulus has to be balanced against the greater thermal stability following free annealing.

**Figure 2.31.** Maximum shrinkage stress vs. annealing temperatures for tapes from Figure 2.30

**Figure 2.32.** Residual tensile modulus vs. temperature of onset of shrinkage, following annealing

Figure 2.32 illustrates this point by comparing the onset of shrinkage stress (defined as the temperature at which shrinkage stress first exceeds 2MPa) with the tensile modulus. If a loss in
tensile modulus of 25% is permissible, tapes can be heat treated during production to prevent significant shrinkage stresses below 130°C.

2.4 Conclusions

The drawing conditions of PP tapes determine the morphology of the polymer, and so control mechanical properties and thermal stability, both of which are required for the application of these tapes into the formation of All-PP composite materials. A summary of these properties is shown in Table 2.5. The polypropylene grades used have been chosen by viscosity matching a suitable range of homopolymers and copolymers, based on rheological analysis and melt flow indexing. This viscosity matching is necessary to achieve a stable, highly drawable uniformly-coated tape.

Semi-crystalline polymers such as polypropylene and polyethylene can be deformed at elevated temperatures below \( T_m \) to increase mechanical properties by orienting inherently stiff molecules in the direction of loading. The tensile moduli of these polymers are controlled by the structure of the amorphous phase, which is responsible for load transfer between crystalline regions loaded in series. This amorphous phase becomes ordered during solid state drawing to provide taut tie molecules between crystal lamellae. An increase in tensile modulus is seen with increasing draw ratio. The tensile strength of highly drawn tapes is more dependent on crystal orientation and macroscopic defects than the amorphous regions, and so strength is less directly linked with draw ratio. Increasing the drawing temperature in the second oven allows some relaxation to occur during tape drawing so that a decrease in tensile modulus is seen with increasing drawing temperature. Investigation of the thermal shrinkage behaviour of these tapes has shown that shrinkage is controlled by the same tie molecules that lend the high moduli to the tapes, and so mechanisms that lead to a reduction in shrinkage also have a dramatic effect on the modulus of the tapes. The transverse strength of the tapes, as determined by trouser tear tests, has showed a uniform (low) tear resistance regardless of draw ratio.

### Table 2.5. Summary of PP tape drawing parameters

<table>
<thead>
<tr>
<th>Property</th>
<th>( \lambda \leq 9 )</th>
<th>( \lambda &gt; 9 )</th>
<th>( \lambda = \text{constant} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structural Change</td>
<td>Orientation of crystalline and amorphous regions</td>
<td>Mainly orientation of amorphous regions</td>
<td>Relaxation of amorphous regions</td>
</tr>
<tr>
<td>Density</td>
<td>▼</td>
<td>▲</td>
<td>▼</td>
</tr>
<tr>
<td>Modulus</td>
<td>▲</td>
<td>▲</td>
<td>▼</td>
</tr>
<tr>
<td>Strength</td>
<td>▲</td>
<td>▲</td>
<td>▼</td>
</tr>
<tr>
<td>Strain to Failure</td>
<td>▲</td>
<td>▲</td>
<td>▼</td>
</tr>
<tr>
<td>Shrinkage Stress</td>
<td>▲</td>
<td>▲</td>
<td>▼</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>▲</td>
<td>▲</td>
<td>▼</td>
</tr>
<tr>
<td>Onset of Shrinkage</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
</tr>
<tr>
<td>Tear Strength</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
</tr>
</tbody>
</table>

\( \uparrow / \downarrow \) = Property increases/decreases  
\( = \) = Property is unaffected
Chapter 3

Tailoring the Interfacial Properties of All-PP Composites

3.1 Introduction

In the previous chapter, it was shown possible to create highly oriented polypropylene tapes, with high tensile strength and stiffness, by solid state drawing. However, in order to consolidate these tapes into a coherent All-PP composite, the effect of the tape manufacture and consolidation parameters on the interfacial properties of these tapes must be investigated. The interfacial properties of composites are responsible for many of the failure modes of composite systems. These interfacial properties of a composite are commonly investigated using microcomposite systems, to isolate failure modes and the understanding of these failure modes can then be applied to predict the failure of real composite systems. The polypropylene tapes in this research are co-extruded to carry the matrix and the reinforcement in one unit, and so optimisation of both the homopolymer (reinforcement) layer for high mechanical properties and the copolymer (matrix) layer for good interfacial strength must be considered simultaneously. The previous chapter showed that the choice of parameters applied in the extrusion and drawing of these tapes determines the mechanical properties of the tapes. These same parameters also affect the strength of the interfaces formed when these tapes are bonded to each other in a composite system.

3.1.1 Autohesion of Polymers

To optimise the interfacial strengths of All-PP composites, it is important to understand the mechanism of autohesion which controls the bond strength between adjacent tape surfaces following compaction. If two isotropic polymer surfaces are brought together an interface is formed, which, initially will have no molecules traversing it. At temperatures above the glass transition temperature, but below the viscous (melting) temperature, some molecular mobility is permitted but large scale translation is prevented by the presence of neighbouring molecules and molecular entanglements (see Chapter 1). However, interdiffusion of molecules occurs over time and can be described by considering a reptation model (de Gennes, 1971).
A polymer molecule of finite length can be considered to be fixed in a hypothetical tube, imposed by neighbouring molecules, as shown in Figure 3.1i. Microbrownian motion leads to movement back and forth along the molecular axis (through the tube) and with each movement, the prominent end assumes a random conformation. After time, $t_1$, with each back and forth motion through the tube, the amount of the original hypothetical tube is shortened incrementally (see Figure 3.1ii). Later, at time $t_2$, the amount of the original tube remaining becomes very short, as shown in Figure 3.1iii, and ultimately the original tube is destroyed altogether. The polymer molecule has now moved from its original location, although is still equally fixed by a new hypothetical tube composed of new neighbouring molecules. The time taken for a molecule to escape its initial tube and move to a completely new tube is defined as the reptation time, $t_R$, and scales with molecular weight, $M_w$,

$$t_R \propto M_w^3$$

This reptation time describes the movement of a polymer molecule to a new, random location. Since all molecules are moving simultaneously, after this time interdiffusion will completely remove an interface between two polymer surfaces since molecules near the interface will move to new random hypothetical tubes and some of these will traverse the interface (see Figure 3.2). On initial contact, there is no means to transfer load across the interface so it is a structural weak point. The strength of the interface increases as molecules diffuse across the interface until $t_R$ is reached, and the interface strength reaches the cohesive strength of the polymer. From equation 3.1, it can be seen that low molecular weight polymers are ideal for rapid diffusion. However, lower molecular weight polymers also have lower cohesive strengths, and so the resulting bond has a lower maximum strength.

As with other diffusion processes (see Chapter 5), reptation times scales exponentially with absolute temperature (Wool, 1983), and so $t_R$ decreases with increasing temperature. These models ignore the presence of the crystalline component in semi-crystalline polymers. These crystalline regions will act as obstacles to molecular movement, and so increase reptation time at lower temperatures.
However, since the bonding being investigated here occurs at elevated temperatures, i.e. near to the melting temperature of the copolymer, it is likely that the any effect due to the crystalline phase impeding interdiffusion would be small and can be ignored (Xue, 1997). During the co-extrusion of All-PP tapes, bonding between copolymer and homopolymer layers is excellent since the melt possesses high molecular mobility which allows rapid diffusion. However, it is important to describe the bond between two neighbouring copolymer layers that will occur when two adjacent tapes are brought together during composite production.

\[ \Delta G = \Delta H - T\Delta S \]  

Where \( \Delta G \) = Gibbs free energy difference between crystal and liquid  
\( \Delta H \) = Enthalpy difference between crystal and liquid  
\( \Delta S \) = Entropy difference between crystal and liquid

At the crystal melting temperature, \( T=T_m \), there is thermodynamic equilibrium between crystalline polymer and the melt. Therefore, \( \Delta G=0 \), so:

\[ T_m = \frac{\Delta H}{\Delta S} \]

From equation 3.3, it is clear that increasing the molecular orientation of a polymer by drawing and the resulting decrease in entropy causes an increase in the melting temperature. Until now, maximum molecular orientation has been the target for a co-extruded tape to achieve high mechanical properties. However, during drawing, both the copolymer and the homopolymer are subject to this molecular orientation. From equation 3.3, the effect of this molecular orientation on
the copolymer would be an increase in melting temperature. This will adversely affect the ability of the tapes to bond at the lower end of the compaction temperature range, by hindering interdiffusion.

In a highly oriented polymer, the increased molecular alignment will also reduce molecular freedom. Since the co-extruded polymer tapes are constrained during consolidation to preserve orientation, a highly oriented copolymer layer will also experience a constraining affect and a further increase in melting temperature, as described previously (see Figure 1.20). Thus it is desirable to achieve high orientation in the homopolymer layer and high mechanical properties, but also to retain isotropy in the copolymer layer to facilitate autohesion. The ideal co-extruded tape for All-PP composite production is proposed in Table 3.1.

In order to promote rapid cycle times in composite part production, it is not feasible to achieve autohesion between tapes by using large time scales. Therefore the adhesion between co-extruded tapes must be achieved by heating the tapes to temperatures close, to or exceeding, the melting temperature of the copolymer layer. Therefore, there is a balance between processing All-PP composites at such high temperatures which allow complete autohesion of adjacent tapes, and processing at low enough temperatures to prevent molecular relaxation of the highly oriented tapes.

<table>
<thead>
<tr>
<th>Component</th>
<th>Structure</th>
<th>Molecular Schematic</th>
<th>Entropy</th>
<th>( T_m )</th>
<th>Tensile Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer</td>
<td>Highly oriented</td>
<td>![Homopolymer Schematic]</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Copolymer</td>
<td>Isotropic</td>
<td>![Copolymer Schematic]</td>
<td>High</td>
<td>Low</td>
<td>Unimportant (Low volume fraction)</td>
</tr>
</tbody>
</table>

The main focus of this chapter is to investigate the effect of tape production and compaction conditions on the interfacial properties of co-extruded tapes. The effects investigated here are tape draw ratio, copolymer layer thickness, compaction temperature, and tape drawing temperature. Subsequently, the interfacial properties of tape in a fabric form will be investigated.

### 3.2 Experimental Procedure

The interfacial strength of All-PP composites is determined by bonding co-extruded PP tapes created using an R&D co-extrusion line fitted with two post-drawing ovens, at Lankhorst Indutech BV, Netherlands (see Figure 2.5). These tapes are bonded by applying heat to facilitate interdiffusion of copolymer molecules across the interface, and then this interface is then pulled apart to determine the strength of the bond.
The polymers used for co-extrusion are shown in Table 2.4, and were selected with similar viscosity, as discussed in Chapter 2. The tapes are co-extruded to possess a A:B:A (copolymer:homopolymer:copolymer) structure as shown in Figure 3.3; here a cross section of an undrawn co-extruded tape is shown for clarity, and the homopolymer layer is clearly seen as the central white region, while the thin copolymer layer on either side is seen in black. In this image, the copolymer appears black due to the addition of carbon black to aid visualisation. The drawing direction is out of the plane of the paper.

In addition to the carbon black, small percentages of UV stabiliser are also added to the copolymer layer, but these additives in small quantities are kept constant throughout this research. Preliminary studies revealed that the presence of these additives did not affect the interfacial performance of these tapes. Before drawing, typical tape dimensions are 4cm wide x 0.5 mm thick, although these initial tapes are cut into small tapes with typical widths of 4mm to be drawn. The greatest proportion of the tape is the homopolymer layer, which is the highly oriented structural component of the tape. The copolymer layer is present to facilitate bonding of the tapes to each other during composite compaction and so a minimum continual thickness of copolymer layer is desired to achieve maximum volume fraction of reinforcement in the final composite. The proportion of these layers can be controlled simply by altering the relative outputs of the A and B extruders. Typically these tapes have dimensions of 2~4.5mm width and 60~125µm depending on the draw ratio, \( \lambda \). The tape can then be woven into a plain weave fabric typically with an areal density of \(~100g/m^2\), although it was not viable to create woven tape fabric from the entire range of tapes produced. The range of tapes produced for interfacial investigations are summarised in Table 3.2.

The nomenclature used to identify the tapes is described as:

\[
x - y - (z)
\]

Where

\[x\] = Draw ratio
\[y\] = Approximate total percentage copolymer layer
\[z\] = Drawing temperature (where altered)
To suitably determine the bonding characteristics of a wide range of different tapes, it is not feasible to create composite plates for every tape material. Therefore, test methods were devised to determine the interfacial strengths of individual tapes through the creation of ‘microcomposites’ which are designed to provide information about a particular interlaminar failure mode. Based on this data, the experiments can then be scaled up to woven tape fabric specimens, which are closer to real composite systems.

### 3.2.1 DSC Measurement

To determine the melting temperatures of both the homopolymer and copolymer components of the tape, differential scanning calorimetry (DSC) was performed on 5mg samples of polymer taken from the pellet form, using a TA Instruments DSC Q1000 differential scanning calorimeter. To remove the effect of thermal history on the DSC results, samples were heated in the DSC from ambient temperature to 180°C at 10°C.min⁻¹ and then cooled back to 20°C, also at 10°C.min⁻¹. Immediately, the samples were reheated to 180°C at 10°C.min⁻¹ and the endothermic data taken from this second heating stage. The data obtained from this method describes the crystalline melting temperature, which is shown as a peak endotherm.

### 3.2.2 T-Peel Testing of Tape Microcomposite

In this research two interfacial failure modes have been investigated: T-peel tests have been performed to determine the tapes’ resistance to failure by peeling (mode I failure), and single lap shear tests have been performed to determine the tapes’ resistance to mode II (shear) failure. T-Peel tests were performed on a variety of tapes to determine the effect of draw ratio, copolymer layer thickness, relative copolymer:homopolymer proportion and drawing temperature on the peeling

<table>
<thead>
<tr>
<th>Tape Name</th>
<th>Draw Ratio</th>
<th>Relative Tape Configuration</th>
<th>Copolymer Layer (total)</th>
<th>Copolymer Layer Thickness (each side)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-8</td>
<td>4</td>
<td>4.2:91.6:4.2</td>
<td>8.4%</td>
<td>5.25</td>
</tr>
<tr>
<td>6-8</td>
<td>6</td>
<td>4.2:91.6:4.2</td>
<td>8.4%</td>
<td>4.02</td>
</tr>
<tr>
<td>9-8</td>
<td>9.33</td>
<td>4.2:91.6:4.2</td>
<td>8.4%</td>
<td>3.35</td>
</tr>
<tr>
<td>12-8</td>
<td>12</td>
<td>4.2:91.6:4.2</td>
<td>8.4%</td>
<td>3.04</td>
</tr>
<tr>
<td>14-8</td>
<td>14</td>
<td>4.2:91.6:4.2</td>
<td>8.4%</td>
<td>2.86</td>
</tr>
<tr>
<td>15-8</td>
<td>15</td>
<td>4.2:91.6:4.2</td>
<td>8.4%</td>
<td>2.83</td>
</tr>
<tr>
<td>14-15</td>
<td>14</td>
<td>7.7:84.6:7.7</td>
<td>15.4%</td>
<td>5.67</td>
</tr>
<tr>
<td>14-18</td>
<td>14</td>
<td>9.3:81.4:9.3</td>
<td>18.6%</td>
<td>7.12</td>
</tr>
<tr>
<td>14-24</td>
<td>14</td>
<td>12.1:75.8:12.1</td>
<td>24.2%</td>
<td>9.18</td>
</tr>
<tr>
<td>13-21(160)</td>
<td>13</td>
<td>10.8:78.4:10.8</td>
<td>21.6%</td>
<td>7.61</td>
</tr>
<tr>
<td>13-21(170)</td>
<td>13</td>
<td>10.8:78.4:10.8</td>
<td>21.6%</td>
<td>7.61</td>
</tr>
<tr>
<td>13-21(180)</td>
<td>13</td>
<td>10.8:78.4:10.8</td>
<td>21.6%</td>
<td>7.61</td>
</tr>
<tr>
<td>13-21(190)</td>
<td>13</td>
<td>10.8:78.4:10.8</td>
<td>21.6%</td>
<td>7.61</td>
</tr>
</tbody>
</table>
strength. The T-peel test specimens are composed of two pieces of tape welded together by heating, and then a non-welded region is used to start peeling the welded tapes apart along the weld zone at an angle of 180°. This is illustrated in Figure 3.4.

Creating micro composite specimens using production methods used for All-PP composites are problematic due to the small size of the specimens involved. The hot press used for subsequent composite production lacked the accuracy of pressure to provide suitably low pressure to weld the tapes without totally deforming the specimens. To overcome this problem, a new method of creating T-peel test specimens was developed for this research. Polypropylene tapes were twice wound around a steel pipe, both ends secured with heat-resistant adhesive tape (see Figure 3.5), and placed in an oven which has been preheated to the desired temperature. The temperatures of the steel pipe and the circulating air are monitored by two PT100 temperature probes. Once the steel pipe has reached the air temperature, the specimens are held at temperature for 5 minutes. This gave a total duration of 15 minutes in the oven. As the pipe temperature increases, the PP tapes exert a circumferential force due to longitudinal shrinkage of the oriented microstructure. This shrinkage is prevented by constraining the PP tapes at either end by the adhesive tape, and also opposed by a radial thermal expansion of the steel pipe.

![Figure 3.4. Schematic of microcomposite T-peel specimen](image1)

![Figure 3.5. Schematic of tape winding for the production of tape microcomposites](image2)
Thus the tape is constrained longitudinally during heating. As the desired welding temperature is achieved, the two adjacent copolymer layers of the neighbouring tapes are bonded to one another, while the homopolymer layer is prevented from relaxing by the longitudinal constraining. After heating, the pipe is removed from the oven and quenched in cold water, and the bonded tape is removed from the pipe. This ‘hoop’ of tape is then cut to provide two adjacent tape ends which are used for test initiation.

T-peel tests are performed in accordance with ASTM 1876; peeling is performed in a Hounsfield tensile testing machine fitted with a 5N load cell, appropriate grips and a data acquisition computer running QMat tensile testing software. The crosshead displacement causes the two bonded tapes to peel apart in a mode I failure. The tests were performed at crosshead displacement of 5mm.min\(^{-1}\), and each test was repeated at least 5 times to ensure reproducibility. Due to the variation in failure modes seen, some tests required further repetition to be sure that the test results accurately reflect the T-peel strength. The values presented for peel force are defined as the force per unit width of tape required to peel the tapes apart, since this tends to a constant value during peeling.

3.2.3 Single Lap Shear Testing of Tape Microcomposites

Single lap shear tape specimens are created using a similar method. Tapes are wound around a steel pipe as before, but in this case with a heat-proof PTFE film acting as a barrier between certain regions the two wound tapes. The tapes will not bond where the PTFE barrier prevents contact, and so the bonded area (lap) can be controlled. The single lap shear specimens are tested similarly to the T-peel specimens except that opposite ends of the bonded regions are pulled apart, so that a mode II failure is caused (see Figure 3.6). Lap shear tests were performed using a displacement rate of

![Figure 3.6. Schematic of microcomposite single lap shear specimen](image)
250mm.min\(^{-1}\) applied using the same test set-up as described for T-peel testing. Due to the higher loads involved in single lap shear testing, a 1kN load cell was used.

### 3.2.4 Maximum Shear Stress Determination

The shear strength of the copolymer between two bonded tapes determines the optimum performance of a single lap shear specimen since failure is expected in shear. The shear strength of a polymer can be determined from the Von Mises criterion. This criterion defines that yielding of a ductile material under a general state of stress will occur when the density of a shear strain energy equals the density of the shear strain energy of the same material loaded in tension at the yield point (Fenner, 1989). The yield stress can be related to the principle stress by equation 3.4.

\[
2\sigma_y^2 = (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2
\]

Where \(\sigma_1, \sigma_2, \sigma_3\) = Principle stresses
\(\sigma_y\) = Yield stress

In the case of pure shear,
\[
\sigma_3 = -\sigma_1 = \tau_{\text{max}}
\]
\(\sigma_2 = 0\)

Where \(\tau_{\text{max}}\) = Shear strength

The maximum shear stress of a material is then given by

\[
\tau_{\text{max}} = \frac{\sigma_y}{\sqrt{3}}
\]

In order to determine the optimum shear strength of single lap shear specimens, the yield strength of the copolymer was established by performing tensile tests on plates formed by melting copolymer pellets in closed mould. Tensile dumbbell shaped specimens of gauge length 20mm and cross sectional area 6 x 1mm were tested in an Instron tensile testing machine fitted with a 1kN load cell and standard grips, at a crosshead displacement speed of 50mm.min\(^{-1}\). A yielding behaviour was clearly seen (see Figure 3.26) and the stress at which this occurred is taken as the yield stress of the polymer. The test was repeated 5 times to ensure reproducibility.

### 3.2.5 T-Peel Testing of Fabric Composites

In addition to single tape T-peel specimens, specimens are also created using \([0^\circ/90^\circ]\) plain weave fabric. This failure behaviour more directly simulates peeling failure in a composite system. Specimens are created by stacking two layers of fabric in a close fitting mould (see Figure 4.5) which are then consolidated by the application of heat and pressure. Again, a PTFE film is used as a barrier to limit bonding of the sheets to areas required to initiate peeling (see Figure 3.7). This stacked two fabric ply sheet is then cut into strips with a width of 25mm and a T-peel test is performed at a crosshead speed of 250mm.min\(^{-1}\). Fabric T-peel tests have been performed at \(0^\circ/90^\circ\)
and $\pm 45^\circ$ to the tape direction. An extra sheet of PTFE is placed above the fabric plies to give uniform thickness to the specimen and ensure even pressure distribution.

![Figure 3.7. Stacking sequence for the creation of fabric T-peel test specimens](image)

### 3.2.6 Lap Shear Testing of Fabric Composites

To model the lap shear strength within a composite system, woven tape specimens were made by compacting stacked plies of fabric. Parallel cuts were placed in each ply along one tape direction, prior to compacting. These cuts were equally spaced in each ply by a distance $x$ apart, and alternate layers were shifted by a distance $x/2$ normal to the cutting the cutting direction. This gave an arrangement as presented in Figure 3.8. When this system is compacted, the result is a composite plate with regular short tapes of length $x$ aligned in one tape direction, running perpendicular to the cutting direction. These tapes are overlap with a regular length of $x/2$. The plates are cut into tensile testing strips perpendicular to the cutting direction and are tested to tensile failure in an Instron tensile testing machine equipped with a 5kN load cell and composite grips.

Plates were manufactured with tape overlap length, $x$, = 8.8mm, 13mm, 18mm, 20mm, 30mm and 40mm, and each plate yielded 5 tensile test specimens. The tensile test specimens measured 15mm wide and 0.9mm thick; a gauge length of 120mm and a cross head speed of 10mm.min$^{-1}$ were used. Each plate was composed of 6 plies, and were compacted at a temperature of 145°C and a pressure of 3.6MPa. Further details on the processing of composite plates from woven tape fabric can be found in Chapter 4.

Since the case of fabric lap shear tests are slightly more complex than the single tape lap shear tests, the derivation of the debond strength, $S$, is described by equation 3.6.

$$S = \frac{F}{w(n-1)}$$  \hspace{1cm} 3.6

Where

- $S$ = Debond strength per unit width [N.mm$^{-1}$]
- $F$ = Load at failure
- $w$ = Width of specimen
- $n$ = Number of plies
Since this strength is based on stacked plies, there will be $n-1$ bonded interfaces in a stack of $n$ plies.

3.3 Results and Discussion

3.3.1 Thermal Properties of Polymers Used for Tape Production

To understand the thermal properties of the polymer grades used in tape production, DSC traces were recorded as described above. Figure 3.9 shows the DSC traces of the homopolymer blend and the random copolymer, C2 (see Table 2.4). Copolymer C2 is a random block polypropylene copolymer containing approximately 6% w/w ethylene. The traces are shifted vertically for clarity.
The copolymer has a very broad melting peak, with the first maximum at 107°C. This reflects the ‘sealing initiation temperature’ of 106°C published by the manufacturer (Basell, 2004), and so adhesion would be expected to be attainable within a short time scale i.e. seconds, at this temperature, although the experimental determination of the sealing temperature by the manufacturer is unclear. The homopolymer blend shows a much narrower melting peak at 160°C, and so the melting behaviour is much more closely defined. However, the thermal stability of the tape was investigated in Chapter 2, and since molecular relaxation occurs at temperatures far below the melting temperatures of the homopolymer, the melting temperature of the homopolymer is not directly relevant to composite production.

3.3.2 The Effect of Draw Ratio on T-Peel Strength of Tape Microcomposites

T-peel tests performed on tape microcomposites provide useful information about mode and location of failure, as well as peel strength. The parameters varied in this chapter are tape draw ratio, compaction temperature and copolymer layer thickness, as described in Table 3.2. Figure 3.10 shows the effect of compaction temperature on the T-peel force of a range of tapes created with identical composition, but varying draw ratio and compaction temperature. In these first tapes, it is clear that there is an increase in peel force with increasing compaction temperature and a decrease in peel force with increasing draw ratio. There is also a noticeable shift in the onset of adhesion with increasing draw ratio, but even for lowest draw ratio tape, there onset of adhesion is 15°C higher than the initial melt peak of the copolymer pellet (see Figure 3.9).

![Figure 3.10. Peel force vs. compaction temperature for tapes with increasing draw ratio and constant percentage copolymer](image-url)
The onset adhesion temperature is a most important factor because this minimum temperature required for the onset of adhesion will define the compaction processing window applicable to the final composite. The lowest possible temperature for the onset of adhesion defines the lower limit of the temperature processing window for the manufacture of All-PP composites; the upper limit of this processing window is governed by the temperature at which the tape relaxes. Tapes 4-8 and 6-8 ($\lambda = 4$ and 6, respectively) show very similar behaviour, and there is a clear transition to a much lower peel force when $\lambda > 6$. This also coincides with the creation of microvoids, as described in Chapter 2.

3.3.3 The Effect of Copolymer Layer Thickness on T-Peel Strength of Tape Microcomposites

The increase in the minimum temperature for the onset of adhesion with increasing draw ratio could be due either to an effect of the drawing process on the structure of the copolymer layer or by the reduced thickness of copolymer layer as a consequence of drawing. Figure 3.11 shows the effect of altering the copolymer layer thickness in tapes with the same draw ratio. Tapes 14-8, 14-15, 14-18 and 14-24, possess increasing proportions of copolymer layer with constant proportion of copolymer, and it is clear that there is little difference in either the onset of adhesion or the levels of peel strengths obtained. It seems that the minimum proportion of copolymer layer required to obtain good peel strength between two parallel tapes is below the thicknesses of the tapes investigated in this study. Figure 3.11 also suggests that since all these tapes show very similar peel strength, the difference in peel strength seen in Figure 3.10 must be related to the drawing of the tapes, rather than the dimensions of the copolymer layer.

![Figure 3.11. Peel force vs. compaction temperature for tapes with increasing draw ratio](image)

Figure 3.12 shows the same data that has been presented in Figure 3.10, as a function of draw ratio. The lines on the graph represent lines of equal compaction temperature. Again, the transition in peel force as $\lambda > 6$ is seen. The high peel strength of tapes with lower draw ratios is of less interest to this
research due to the lower stiffness and strength of such tapes. The tapes with lower draw ratios exhibit higher standard deviation in recorded peel force. This is because, during specimen production, the thicker copolymer layers of low draw ratio tapes effectively lubricate adjacent tapes, allowing relaxation and encouraging melting of the tape.

**Figure 3.12.** Peel force vs. draw ratio for tapes with increasing draw ratio

**Figure 3.13.** Peel force vs. copolymer layer thickness for tapes with increasing draw ratio
The actual copolymer layer thicknesses due to increasing draw ratio are seen in Figure 3.13 for tapes 4-8, 6-8, 9-8, 12-8, 14-8 and 15-8, with constant compaction temperatures. Once again, it can be seen that with increasing draw ratio there is a decrease in peel strength. However, Figure 3.14 shows that the relative thickness of copolymer layer for tapes 14-8, 14-15, 14-18 and 14-24, causes no significant change in peel strength despite a wide range of copolymer layer thicknesses. This proves that the onset of adhesion and the maximum level of peel strength seen is not due to either the relative proportion of copolymer layer on the tapes or the absolute thicknesses of copolymer layer.

3.3.4 The Effect of Drawing Temperature on the T-Peel Strength of Tape Microcomposites

In Chapter 2, the effect of increasing the second oven drawing temperature on the mechanical properties of the tapes was described. Figure 3.15 shows the effect of this increase of drawing temperature on the peel properties of 4 tapes with the same composition. There is a shift in the onset of adhesion to lower bonding temperatures with increasing second oven drawing temperature. There is also an increase in the maximum peel strength for these tapes. As drawing temperature in the second oven is increased, increased relaxation is seen in the orientation of the tapes. This is seen as a decrease in tensile modulus (see Figure 2.22), and also appears here as an increase in the maximum peel strength of the tape. Just as increasing draw ratio causes greater orientation which reduces the cohesive (transverse) strength of the tape, increasing the drawing temperature relaxes the orientation and reduces the amount of fibrillation in the tape. This can also be seen from the transition from an opaque tape appearance to a transparent tape appearance with increasing drawing temperature (see Figure 2.19). Therefore the cohesive strength, which limits maximum peel strength, increases.
The increase in onset of adhesive can also be explained by a similar mechanism. During drawing, orientation is achieved in the homopolymer because the tapes are drawn at an optimum temperature for the homopolymer which allows enough molecular movement to allow alignment of tie molecules between crystalline lamellae, but insufficient movement to allow total flow which would lead to tape breakage in the drawing line. Preliminary studies (Schimanski, 2002) provided this optimum temperature based on achieving the highest tensile stiffness in mono-extruded homopolymer tapes. The temperature used to promote the correct degree of molecular movement is relative to the melting temperature of the homopolymer.

**Figure 3.15.** Peel force vs. compaction temperature for tapes with increasing drawing temperature

Samples a and b are highlighted and shown in further detail in Figure 3.16

**Figure 3.16.** Optical micrographs of peel surfaces taken from samples a and b as shown in Figure 3.15, indicating the effect of drawing temperature on tapes compacted at the same temperature.
During compaction, the melting temperature of the homopolymer is artificially raised by lateral constraining; this prevents shrinkage and relaxation of the microstructure (see Figure 1.20). However, during compaction it is necessary for the copolymer to melt in order to provide bonding between adjacent tapes. Therefore it is advantageous for the copolymer to be unoriented. Since the homopolymer and copolymer layers are drawn as one tape during tape production, and the copolymer is present in a very thin film on the homopolymer core, it is likely that the copolymer will be oriented along with the homopolymer. Thus when the resulting tape is constrained, it is likely that the overheating by constraining technique will apply to increase the melting temperature of homopolymer and copolymer. This explains the fact that the onset of adhesion in highly drawn tapes ($\lambda>6$) bonded so far, occurs above the melting temperature of the copolymer ($T_m=140^\circ C$).

This effect can be reduced by increasing the drawing temperature in the second oven. The temperature in the first oven is not a major concern here, as this needs to be far below the melting temperature of the tapes to facilitate further drawing in the second drawing stage. Since the melting temperature of the copolymer is less than that of the homopolymer, it is possible to draw the entire tape at a temperature high enough to allow maximum relaxation of the copolymer, while allowing minimum relaxation, and so, loss in tensile properties, of the homopolymer.

In Figure 3.17 a model of the effect of increasing drawing temperature on interfacial strength is shown, it can be seen that increasing the drawing temperature increases the cohesive peel strength and also decreases the temperature of the onset of adhesion. This seems a very positive step for the potential production of All-PP composites, as the temperature processing window is widened to facilitate compaction at lower temperature extremes. However, this superior adhesion has to be balanced against the loss in mechanical properties resulting from drawing at a higher drawing temperature. Combining data from Figures 2.22 and 3.15, gives Figure 3.18. Tape 13-21(160) did not show a cohesive strength in Figure 3.15 but the cohesive strength can be predicted from Figure 3.18 to be $\sim 26 N mm^{-1}$.

**Figure 3.17. The effect of drawing temperature on the cohesive strength and onset of adhesion in All-PP microcomposites**
Since the improved peel strength is matched with decreased tensile modulus, the exact optimum tape drawing temperature depends on final composite application. If composite processing techniques can be optimised to reduce the importance of a low onset of adhesion, the optimum tape drawing temperature will shift towards lower drawing temperatures and the resulting higher mechanical property tape. Conversely, if composite adhesion is required at these very low temperatures, a decrease in tensile modulus is the penalty for this lower temperature adhesion. The cohesive strength seen in tape 13-21(190) is the maximum possible for this draw ratio, since drawing tapes above this temperature (190°C) resulted in frequent tape breakage in the oven.

![Graph showing cohesive peel strength and tensile modulus of tapes drawn with increasing drawing temperature](image)

**Figure 3.18.** Cohesive peel strength and tensile modulus of tapes drawn with increasing drawing temperature

### 3.3.5 T-Peel Failure Modes in Microcomposites

During the experimental research it was noted from these tests that the compaction temperature controls the measured peel force and so also the location of failure of the tapes (see Figure 3.16). The interfacial failure can be seen to occur in three regions of the tape, as shown in Figure 3.19: (a) adhesive failure between two adjacent layers of copolymer, (b) a combination of adhesive failure between adjacent copolymer layers and cohesive failure within the oriented homopolymer layer, and (c) cohesive failure within one of the oriented homopolymer layers. Generally, at lower temperatures (below the crystalline melting point of the copolymer layer) the copolymer layer begins to become ‘tacky’ as interdiffusion starts to occur (see Figure 3.9), bonding of the tapes is weak and in peeling, adhesive failure is seen between the two adjacent copolymer layers. As compaction temperature is increased, the adjacent copolymer layers fuse together and molecular diffusion causes a combination of failure within the copolymer layer and within the homopolymer layer. This involves an increase in recorded peel force. As the compaction temperature is increased further, the adjacent copolymer layers are allowed to melt and excellent bonding is seen between the two adjacent copolymer layers and also the surface of the homopolymer layer.
Figure 3.19. SEM images of different failure modes in bonded tapes

a. Adhesive failure mode

b. Transition from adhesive to cohesive failure mode

c. Cohesive failure mode

PP homopolymer microfibrils

Figure 3.19. SEM images of different failure modes in bonded tapes
Failure in peeling now occurs through a cohesive failure mode within the highly oriented homopolymer layer. This is due to the high orientation of the homopolymer layer which develops a highly anisotropic, fibrillar structure in the drawing process (Peterlin, 1971). As draw ratio increases, the volume fraction of polymer molecules oriented transverse to the drawing direction decreases. This means that the transverse strength of the tape also decreases since strength of the tape in a given direction is due to the proportion of molecules oriented in that direction. In Chapter 2 of this thesis, the effect of molecular orientation on transverse strength was investigated by trouser tear tests. These proved inconclusive since the crack had to cross the tough copolymer layer which increases the tear resistance and will obscure any possible effect of the increased orientation on the transverse strength of the homopolymer core. The decrease in cohesive strength shown in Figure 3.18 clearly reveals the decrease in transverse strength due to increasing molecular orientation of the homopolymer core. Hence a highly drawn tape possesses very high tensile strength in the drawing direction but very low transverse strength, since the exploitation of strong covalent bonds in the drawing direction leaves only weak van der Waals acting in the transverse direction.

In addition to this orientation factor is the presence of microvoids; a highly oriented tape can be considered to be a bundle of microfibrils held together by few intrafibrillar tie molecules and weak van der Waals attraction. As the adhesion between neighbouring tapes improves, the adhesive strength of the bond exceeds the cohesive strength of the homopolymer layer and so failure moves from an adhesive failure of the copolymer layers to a cohesive failure of one of the homopolymer layers. The cohesive strength of a tape decreases with increasing draw ratio due to orientation, and so the maximum peel strength of a tape also decreases with increasing draw ratio. For tapes with a constant draw ratio, increasing compaction temperature rapidly increases the adhesive strength until it exceeds the cohesive strength of the oriented tape and so the maximum achievable peel force, the cohesive peel force, is reached.

The relationship between failure location and peel strength is illustrated by test specimens which show transitional failure behaviour. This transition is accompanied by a fluctuation in the recorded peel force of the tape. One such event is presented here: a force displacement curve, Figure 3.21a, a composite photo of one of the peel surfaces, Figure 3.21b, and a schematic showing the crack path through the thickness of the specimen, Figure 3.21c. In part 3.21b the microfibrils are clearly visible on the surface of the tape, and tape thickness measurements confirm the crack path as described in Figure 3.21c. The increase in peel force is clear from 3.21a, with the peel force increasing by almost 3 times during failure in a cohesive failure mode. This is due to the higher energy involved in pulling large numbers of microfibrils from the homopolymer layer.

The peel strength of tapes can be simplified to a model shown in Figure 3.20. Bonding starts at an onset temperature dependent on the melting temperature and the degree of orientation of the copolymer used. Peel strength increases with temperature as higher temperatures allow better adhesive bonding. Ultimately, the cohesive strength of the highly oriented component of the tape is reached, and this limits the peel strength. A further increase in temperature may improve adhesion, but since this has exceeded cohesive strength, it is irrelevant to further failure. As temperature increases further, eventually the melting temperature of the tape will be reached and the entire system will breakdown. These high temperatures are of little interest to All-PP composites since
molecular relaxation will have reduced the tensile properties of the tape before actual melting is approached.

3.3.6 The Effect of Tape Production Parameters on the T-Peel Strength of Woven Fabric Composites

The T-peel tests described here can be equally applied to composite specimens produced by compacting plies of woven fabrics made from co-extruded tapes. This is important as the T-peel strength of two matching tapes is based on the perfect contact between two flat surfaces. In a real composite, this situation is highly unlikely due to the crimping of tapes in when woven into a fabric. Three tapes that have been produced on an industrial drawing line with different production parameters have been woven into plain weave fabrics with an areal density of ~100g.m\(^{-2}\). These three fabrics are summarised in Table 3.3.

Figure 3.22 shows the peel strength of three fabrics 17-10(170), 8-20(160) and 17-10(160). The basic characteristics described previously for the tapes are still present in bonded fabrics. Fabric 17-10(170) shows the lowest onset of adhesion, as the tape used has been processed with the optimum balance of processing parameters found so far for the single tape, i.e. a high draw ratio to provide good mechanical properties and a high drawing temperature to provide good interfacial properties. Fabric 17-10(160) has been produced with a lower drawing temperature to fabric 17 10(170), and the result is a higher onset of adhesion compared to the tape (see Figure 3.16), but at higher temperatures the maximum peel strength is similar. This supports the concept that a slightly higher drawing temperature can reduce the onset temperature for tape adhesion by allowing relaxation in the copolymer layer, but will have a negligible effect on the limiting cohesive strength.
Figure 3.21. Failure location of a single T-Peel specimen: (a) peel force vs. peel length, (b) schematic of peel path and (c) composite photo of peel surface with mm scale increments.
Table 3.3. Woven tape fabrics used for T-peel testing

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<tbody>
<tr>
<td>17-10(170)</td>
<td>17</td>
<td>5:90:5</td>
<td>2.16 x 0.065</td>
<td>170</td>
</tr>
<tr>
<td>8-20(160)</td>
<td>8</td>
<td>10:80:10</td>
<td>3.01 x 0.095</td>
<td>160</td>
</tr>
<tr>
<td>17-10(160)</td>
<td>17</td>
<td>5:90:5</td>
<td>2.16 x 0.065</td>
<td>160</td>
</tr>
</tbody>
</table>

Fabric 8-20(160) is produced at a lower draw ratio ($\lambda=8$) and so lacks the high mechanical stiffness of fabrics 17-10(170) and 17-10(160), but has the greater cohesive strength expected of a low draw ratio tape (1.2 N.mm$^{-1}$). Also shown on Figure 3.22 is data reported in other research (Hine et al., 2003) for mono-extruded PP tape fabrics compacted using the ‘hot compaction’ technique described in section 1.4 of this thesis. Only an optimum compaction temperature is reported by Hine et al for this particular fabric, although other tapes are discussed. This fabric is used for comparison because it is the closest comparison to the fabrics used in this thesis. The relatively low tensile moduli (6.2GPa) of the tapes reported by Hine et al suggest that a low draw ratio tape is used (estimation from Figure 2.17: $\lambda=8$). Since Hine et al use mono-extruded tapes, a bond at this temperature would be very strong and failure should be cohesive as a value of 1.22±3.9 N.mm$^{-1}$ is reported. If this estimated draw ratio is correct, then their data fits well with the data from this thesis. Other publications have also quoted a cohesive peel strength of 1.2 N.mm$^{-1}$ for oriented PP ($\lambda=8$) bonded to aluminium (Chinsirikul et al., 1993). These results support the high cohesive strength seen in lower draw ratio tapes.

Figure 3.22. Peel force vs. compaction temperature for fabrics 17-10(170), 8-20(160) and 17-10(160)

Unlike the T-peel tape specimens, a clear cohesive failure limit is not seen in the T-peel fabric specimens. Since crack propagation is initiated between layers during tape T-peel specimen production, initial failure is adhesive, but the crack rapidly moves to a cohesive failure during
peeling, as shown in the early stages of Figure 3.20. In the case of fabric peeling, the weave geometry prevents this, since the alternating tape direction in a fabric does not allow a constant crack to propagate for long enough to reach a cohesive failure mode, i.e. for every tape width that the fabric is peeled, the weave forces the crack surface back to between fabric plies.

Figure 3.22 presents two data sets for each of fabrics 17-10(170), 8-20(160) and 17-10(160); peel strength in the warp/weft direction [0°/90°] and in the [±45°] direction. Peel force in the [±45°] direction follows a similar behaviour to those measured in the [0°/90°] direction, with a proportional reduction in force. Typical force-time curves for these two types of peeling are shown in Figure 3.23. The force oscillates between two approximately constant values, with the wavelength being approximately equal to one tape width. This suggests that the fabric is peeling in increments; when the local stress exceeds a threshold, the peel front advances one tape width and then stops until stress approaches this threshold. This is analogous to ‘stick-slip’ failure often seen in adhesive bond failure. The force/extension curve for the [±45°] specimens shows a similar behaviour with lower values and lower amplitude of oscillation. Since the oscillation is caused by the transition of 0° peeling to 90° peeling for any path normal to peel direction, this effect is much reduced by the peel front progressing at [±45°] to tape direction (see Figure 3.24).

The applied pressure can affect the interfacial properties as well as the mechanical properties of All-PP composites (see Chapter 4). Figure 3.25 shows the effect of increasing the compaction pressure on the peel strength of woven fabrics. As pressure is increased from 0.1MPa to 2 MPa, there is an increase in peel strength, although the trend is similar. For fabric consolidated at 0.1MPa, there is insufficient pressure to cause the molten copolymer layer to completely fill the interply voids (this will be discussed in more detail in Chapter 4 of this thesis). This reduction in bonded area causes a reduced peel strength of the specimens compacted at 0.1MPa. Figure 3.25 also shows the
effect of using a 10µm film of unoriented PP copolymer between the layers of fabric. The use of this unoriented copolymer interleaf reveals an increase in peel strength but is probably due to toughening of the interface resisting crack propagation rather than an actual increase in adhesion as reported for the tearing of oriented polymers (Sims, 1975). This interleaving effect is also well documented for more traditional composites (Li et al., 1996) as a means to increase interlaminar toughness.

**Figure 3.24.** Schematic of peel direction for peeling at 0°/90° and ±45° to tape direction

Figure 3.11 showed that in the case of tape peel specimens, the volume of copolymer present had no effect on the peel properties. However, tape peel specimens are models with perfect, flat contact between the tapes, and so this is to be expected. However, fabric peel composite show that the addition of a thicker copolymer layer by introducing a copolymer film will increase the peel strength. This increase in peel strength may benefit All-PP composites, but as a non-load bearing component, the copolymer film will reduce tensile properties of the composite proportionally to the volume fraction of the interleaf present.

**Figure 3.25.** Peel force of fabric 17-10(170) vs. compaction temperature for increasing compaction pressure and presence of copolymer interleaf
3.3.7 The Effect of Bond Length on Single Tape Lap Shear Strength

The T-peel test can be used to provide useful information for comparing the mode I failure strength of tapes produced with different processing parameters but this behaviour does not directly translate to the mode II failures which are much more common in real composite systems. A more typical failure in composite systems is via debonding and fibre pull-out since the interfacial strength of traditional composites is usually much less than the tensile or cohesive strength of the reinforcement.

The optimum shear strength between two bonded tapes will be achieved when the shear strength of the interface reaches the shear strength of the isotropic copolymer. At this point, it is assumed that the interface has been removed by interdiffusion. Figure 3.26 shows the stress vs. strain curve for a tensile bar of isotropic copolymer with the yield stress, $\sigma_y$, clearly identified. From this yield strength, the shear strength of the copolymer can be established. Equation 3.5 gives the shear strength of the copolymer as 13.1MPa.

![Stress vs. strain curve of an isotropic copolymer tensile specimen loaded in tension](image)

Figure 3.26. Stress vs. strain curve of an isotropic copolymer tensile specimen loaded in tension

In order to describe the strength of the interface in All-PP composites, microcomposite systems were created as described earlier to determine single lap shear strength of microcomposites. Failure in a shear mode may dominate mechanical properties if the reinforcement of the composite is discontinuous. This may occur by design in short fibre composites, or due to overlapping fabrics or penetrative damage of continuous fibre composites. Microcomposite tests were performed to determine the effects of copolymer layer thickness and compaction temperature on the shear strength of the bond.

Figure 3.27 shows the effects of compaction temperature on bond strength for these single lap shear specimens. The first conclusion from this data is that, as with peel test specimens, the interfacial strength increases with increasing compaction temperature. Each of the tapes shows a similar behaviour. As bonded length increases, the bond strength also increases until a maximum for that particular compaction temperature is achieved. This shows that All-PP systems exhibit a `critical
fibre length’ for a given set of processing conditions (Cox, 1952; Wenig and Scholler, 1991; Hull and Clyne, 1996). This suggests that if the bonded region exceeds a given ‘critical’ length, no further improvement in bond strength will be gained by increasing the bonded length.

This is clearly displayed in Figure 3.27, and the critical single lap bond length for these tapes is approximately 5~7mm. It must be remembered that this value is specific for a single lap shear geometry which is only bonded on one side of the tape specimen, unlike tapes in traditional composite fibre pull-out tests. This gives the minimum length of tape for an efficient reinforcement.
of a single lap bond. Ultimately, the strength of the bond at compaction temperature of 160ºC approaches tensile strength of the tape and so the test is no longer valid. The most efficient bond is at the length of the critical single lap bond length, since bonded length exceeding this is not effective. Figure 3.28 shows the average shear stress of the specimens shown in Figure 3.27. The maximum shear stress seen in Figure 3.28 approaches the maximum shear strength for the copolymer (Figure 3.26), suggesting a high degree of interdiffusion across the interface for specimens compacted at 160ºC.

The bond strengths seen here are typically 2 orders of magnitude greater than those seen in T-peel tests (see Figure 3.10). This reflects the relative ease with which a highly oriented polymer can be fibrillated in peel. Figure 3.29 shows the effect of copolymer layer thickness on single lap bond strength, for specimens consolidated at 160ºC. Tape 14-8 (4.2% copolymer layer on either side) shows much lower bond strength than the other tapes, which have similar properties. This suggests that there is a minimum copolymer layer thickness to provide a good bond strength and this is between that of tape 14-8 (2.86µm) and tape 14-15 (5.67µm). There is a slight decrease in the maximum lap strength from tape 14-15 to tape 14-24, but this is believed to be experimental scatter.

**Figure 3.29.** Single lap bond strength vs. bonded length for tapes with increasing copolymer layer thickness

### 3.3.8 The Effect of Bond Length on Fabric Lap Shear Strength

The single lap shear data obtained so far has been obtained by using a very idealised microcomposite model. In order to obtain information about the lap strength in an actual composite, All-PP plate specimens were manufactured as described earlier. These specimens were tested in tension to failure as before for the single tape specimens. The bond strength of a stacked ply specimen compacted at 145ºC is compared with a single tape model compacted at 140ºC, as shown in Figure 3.30. The difference in temperature can be considered as negligible in this small range. The fabric lap joint
shows approximately twice the strength of the tape lap joint. The greater strength of the fabric bond may be due to the test method; the asymmetric single lap shear of the tape specimens are subject to a peeling force due to a moment being created in loading, while the symmetrical double lap fabric specimens do not have this moment.

The fabric lap joint also shows a much greater ‘critical bond length’. This may be explainable by the highly efficient stress transfer of the neighbouring, flat surfaces of the bonded tapes compared to the uneven surface of bonded fabrics. There may also be a discrepancy between the exact length measured in the case of the fabric and the tape due to shrinkage of the fabric, although this is unlikely to account for the large difference in strengths. These fabric lap shear model composites provide information about the effect of tape length in a short fibre composite, although a clear correlation cannot be made between single lap tape microcomposites and fabric double lap microcomposites.

![Figure 3.30. Single lap bond strength vs. bonded length for fabric and tape compacted at ~140°C](image)

3.4 Conclusions

The interfacial properties of any composite system will depend on the compaction conditions during composite production. This is particularly true of single polymer composites, in which compaction conditions control not only the interfacial strength, but also the residual mechanical properties of the reinforcement.

The interfacial properties of any composite system determine the failure mode. The failure mode in All-PP composites has been shown to be controlled by the manufacturing parameters of the tape and the compaction parameters of the composite. Here microcomposites were employed to investigate a wide range of these parameters.
Chapter 3  
Tailoring the Interfacial Properties of All-PP Composites

The T-peel strength of All-PP composites for a given homopolymer/copolymer combination is determined by the tape draw ratio, the compaction temperature, and the drawing temperature of the tape. The thickness of the copolymer layer did not affect T-peel strength within the range examined. As adhesive strength increases, it rapidly exceeds cohesive strength, showing excellent adhesion. The temperature at which bonding occurs is linked to the drawing temperature in tape production. The temperature processing window for All-PP composites is determined by the difference between the onset of adhesion and the loss of tape properties. In this research, the temperature processing window was seen to be >30°C.

Single lap shear tests showed that All-PP composites exhibit a ‘critical tape length’ of ~7 mm. As compaction temperature increases, better molecular diffusion across the interface leads to increased bond strength, ultimately approaching the shear strength of the copolymer. However, the strength of these bonds reaches the tensile strength of the tape, again showing the possibility to create excellent adhesion between All-PP tapes. The single tape T-peel tests were scaled up into fabric peel tests which showed similar behaviour to the single tape tests. Tape single lap shear tests were scaled up to fabric double lap shear tests, and while the effects of drawing and compaction temperature on interfacial strengths were similar, a direct correlation of results could not be made. Table 3.4 summarises the main effects of tape and composite production parameters on the interfacial properties established in this chapter.

Table 3.4 Control of interfacial properties of tape and fabric by varying production parameters

<table>
<thead>
<tr>
<th>Production Parameter</th>
<th>Temperature Processing Window</th>
<th>Tape Cohesive Strength</th>
<th>Maximum Fabric Interface Strength</th>
</tr>
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<tbody>
<tr>
<td>Increasing Draw Ratio</td>
<td>▲</td>
<td>▼</td>
<td>▼</td>
</tr>
<tr>
<td>Increasing Copolymer</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
</tr>
<tr>
<td>Layer Thickness</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
</tr>
<tr>
<td>Increasing Drawing Temperature</td>
<td>▲</td>
<td>▲</td>
<td>▲</td>
</tr>
<tr>
<td>Increasing Compaction Pressure</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
</tr>
</tbody>
</table>

▲/▼ = Property increases/decreases  
= No effect on property seen
Chapter 4

Mechanical Properties of All-PP Composites

4.1 Introduction

So far it has been shown possible to co-extrude polypropylene tapes with excellent mechanical and interfacial properties that are defined by solid state drawing parameters. In Chapters 2 and 3, the relationship between mechanical and interfacial properties and tape drawing parameters, was established by the characterisation of single tapes or simple microcomposite models. However, these models are limited in assessing the real behaviour of a composite system. In this chapter, the mechanical properties of actual composites will be investigated, with particular reference to the influence of composite processing conditions.

The mechanical properties of highly oriented thermoplastics such as All-PP tapes are dependant on microstructure and so thermomechanical history. The consolidation of co-extruded PP tapes into a coherent composite material requires heating and so it is possible that relaxation and shrinkage of highly oriented regions may occur. In order to limit or prevent this relaxation, it is important to define the parameters used to consolidate a collection of tapes into a coherent load bearing structure. The composite production parameters considered here are temperature and pressure, and even though the effect of temperature on the interfacial properties has been described in the previous chapter, further investigation will define the effect of temperature on the mechanical properties of a composite. In order to make a coherent All-PP composite that possesses a strong interfacial strength and retains the high mechanical properties of the constituent tapes, the following processing conditions must be applied:

i) Sufficient pressure to prevent shrinkage by lateral constraining and encourage good interfacial contact for bonding, but not enough to encourage flow of homopolymer tape, resulting in a loss of properties.

ii) Sufficient temperature to melt the copolymer layer to enable fibre bonding, but not so much as to encourage shrinkage, relaxation or melting of the oriented homopolymer phase.
This theoretical processing window is shown schematically in Figure 4.1, although conflicting processes complicate the exact geometry of the window. As compaction temperature is increased, viscosity of the copolymer decreases and so a lower minimum pressure would be predicted for adequate consolidation. However, as temperature is increased, shrinkage forces in the tapes increase and so greater pressure is required to prevent tape shrinkage (see Figure 2.24). As pressure is increased, the maximum applicable temperature decreases since at high pressures, flow and hence relaxation, is encouraged, and so a combination of high temperature and pressure aids relaxation by lateral flow of the composite in the mould.

![Figure 4.1. Temperature/pressure processing window](image)

Even though Figure 4.1 presents a clearly defined processing window, in reality this is unlikely. Within the processing window, mechanical properties are expected to vary greatly as the microstructural mechanisms of shrinkage and lateral flow compete. By creating composite specimens with woven or unidirectional fibre architectures, the effect of processing at a range of temperatures and pressures on mechanical properties can be established. The mechanical performance of unidirectional composites are particularly important as these allow established laminate analysis theory to predict performance of any stacking sequence of unidirectional plies. The aim of this chapter is to characterise All-PP composite laminates by investigating the tensile strength and modulus, and the compressive strength of unidirectional and woven fabric composites, as a function of composite processing parameters. A summary of the mechanical properties of unidirectional and woven tape composites is presented in tables 4.6 and 4.7 respectively, at the end of this chapter.
4.1.1 Laminate Theory

Creating unidirectional composite plates from highly oriented polypropylene tapes will lead to highly anisotropic composite structures. It has already been shown that the transverse properties of the tapes are very low compared to the longitudinal properties and so is likely to have a strong effect in All-PP composites. The degree of anisotropy is an important consideration in the design of planar structures from any composite system. The behaviour of a composite can be predicted by using laminate theory, considering the mechanical properties of the constituent plies of the composite. In order to collect this information, unidirectional composites are loaded at various angles, $\theta$, to the tape direction, as shown in Figure 4.2.

\[ \frac{1}{E_\theta} = \left[ \frac{1}{E_{11}} \right] \cos^4 \theta + \left[ \frac{1}{G_{12}} - 2 \frac{\nu_{12}}{E_{11}} \right] \cos^2 \theta \sin^2 \theta + \left[ \frac{1}{E_{22}} \right] \sin^4 \theta \]

Figure 4.2. Diagram illustrating $\theta$ for a unidirectional composite

The tensile modulus, $E_\theta$, of a unidirectional laminate loaded at an angle, $\theta$, to the tape direction, can be predicted by equation 4.1 (Hull and Clyne, 1996)

Where $G_{12}$ = Shear modulus
$\nu_{12}$ = Major Poisson ratio
$E_{11}$ = Longitudinal tensile modulus
$E_{22}$ = Transverse tensile modulus
Chapter 4  
Mechanical Properties of All-PP Composites

$E_{11}, E_{22},$ and $\nu_{12}$ can be determined experimentally by performing longitudinal ($\theta=0^\circ$) and transverse ($\theta=90^\circ$) tensile tests on unidirectional composites. If $\theta = 45^\circ$, then equation 4.1 can be rearranged to give:

$$\frac{1}{G_{12}} = \left[\frac{4}{E_{45}}\right] - \left[\frac{1 - 2\nu_{12}}{E_{11}}\right] - \left[\frac{1}{E_{22}}\right]$$

4.2

Thus shear modulus, $G_{12}$, can be determined by testing unidirectional composites loaded at $\theta = 45^\circ$.

The tensile strength, $\sigma_{\theta}$, of a unidirectional composite loaded at an angle, $\theta$, to the tape direction can be predicted using various stress criteria models. Two models will be considered here: the maximum stress criterion and the Tsai-Hill criterion. The maximum stress criterion dictates that there are three discrete failure modes, one of which will be dominant depending on the angle of loading, $\theta$. The weakest of these strengths will thus determine the failure mode of the composite laminate.

For small angles, typically $0^\circ < \theta < 10^\circ$, composite strength, $\sigma_{\theta}$, is controlled by strength in the fibre direction, $\sigma_{11}$,

$$\sigma_{\theta} = \frac{\sigma_{11}}{\cos^2 \theta}$$

4.3a

As $\theta$ increases, $\sigma_{\theta}$ is dominated by intralaminar shear strength, $\tau_{12}$,

$$\sigma_{\theta} = \frac{\tau_{12}}{\cos \theta \sin \theta}$$

4.3b

As $\theta$ approaches $90^\circ$, $\sigma_{\theta}$ is dominated by transverse strength $\sigma_{22}$,

$$\sigma_{\theta} = \frac{\sigma_{22}}{\sin^2 \theta}$$

4.3c

These criteria consider that the three failure modes act in isolation and when the threshold of the weakest failure mode is reached, the specimen fails in this failure mode. However, an adaptation of the von Mises yield criterion has also been applied to transversely isotropic composites. If a unidirectional composite is loaded in the 1 direction:

$$\left(\frac{\sigma_{11}}{\sigma_{11}^*}\right)^2 + \left(\frac{\sigma_{22}}{\sigma_{22}^*}\right)^2 + \left(\frac{\tau_{12}}{\tau_{12}^*}\right)^2 - \frac{\sigma_{11}\sigma_{22}}{\sigma_{11}^*\sigma_{22}^*} = 1$$

4.4

Where

- $\sigma_{11}, \sigma_{22} = \text{Tensile stress in 1 and 2 directions}$
- $\tau_{12} = \text{Shear stress in 12 direction}$
- $* = \text{indicates ultimate stress (strength)}$
This is known as the Tsai-Hill criterion (Azzi and Tsai, 1965). If the left hand side of the equation reaches or exceeds 1, failure will occur. This can occur by any one of the three stresses reaching the ultimate value, as in the maximum stress criterion, or alternatively by a contribution of each failure mode. Thus stresses can combine to bring a single failure criterion below the ultimate stress of each mode. Unlike the maximum stress criterion, the particular failure mode is not identified. In the case of a unidirectional composite loaded at an angle, \( \theta \), to the reinforcement direction, this criterion can be adapted to predict the failure stress based on the longitudinal, transverse and shear strengths, and the loading angle:

\[
\sigma_0 = \left[ \frac{\cos^2 \theta (\cos^2 \theta - \sin^2 \theta)}{\sigma_{11}^2} + \frac{\sin^4 \theta}{\sigma_{22}^2} + \frac{\cos^2 \theta \sin^2 \theta}{\tau_{12}^2} \right]^{1/2}
\]

This equation describes a single failure prediction for \( 0^\circ > \theta > 90^\circ \). The longitudinal and transverse strengths can be simply established experimentally, and the intralaminar shear strength, \( \tau_{12} \), of a unidirectional composite can be approximated by loading a 10° off-axis specimen, and applying equation 4.3b (Chamis and Sinclair, 1977). In principle these laminate formulae can be applied to whole range of composite materials but they have also been successfully applied to highly anisotropic polypropylenes oriented by roll drawing which, due to the microfibrillar nature of highly oriented PP, can be considered as a unidirectional fibre laminate (Peijs, 1993; Chen et al., 1994).

### 4.2 Experimental Procedure

#### 4.2.1 Specimen Preparation

The tape used throughout this section is a co-extruded three layer tape, with an A:B:A (copolymer:homopolymer:copolymer) structure, that was manufactured at Lankhorst Indutech B.V., Netherlands, using a full scale production line. The tape properties are summarised in table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1. Summary of PP tape properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Homopolymer [B]</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Copolymer [A]</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Width</strong></td>
</tr>
<tr>
<td><strong>Thickness</strong></td>
</tr>
<tr>
<td><strong>Density, ( \rho )</strong></td>
</tr>
<tr>
<td><strong>Draw Ratio, ( \lambda )</strong></td>
</tr>
<tr>
<td><strong>Composition, [A:B:A]</strong></td>
</tr>
<tr>
<td><strong>E Modulus</strong></td>
</tr>
<tr>
<td><strong>Strength</strong></td>
</tr>
<tr>
<td><strong>Strain to Failure</strong></td>
</tr>
</tbody>
</table>

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All-PP composites specimens were created from this tape. Unidirectional specimens were created via a filament winding process, by winding tape from a bobbin onto a thin, flat steel plate using a custom built winding machine (see Figure 4.3). This frame is then placed in a matching mould and the tapes are compacted into a unidirectional composite sheet by the application of heat and pressure. The application of pressure acts to consolidate tapes, encourage copolymer flow and prevent shrinkage (see Chapter 1). After consolidation, this sheet is cut from the frame to give two unidirectional laminates (one from either side of the winding plate). A schematic of the winding plate in mould is shown in Figure 4.4. The unidirectional composite sheet formed using this winding method is approximately 120mm x 120mm. These laminates can be cut into tensile testing specimens as described in ASTM 3039. The dimensions of the tensile testing specimens are shown in table 4.3.

Figure 4.3. Schematic of filament winding plate to manufacture unidirectional composites

Figure 4.4. Schematic of close fitting mould used to consolidate unidirectional plates

The 0°/90° woven tape specimens were created using the same tape which has been woven into a balanced, plain weave fabric possessing an areal density of ~100g.m⁻² by BW Industrial B.V., Netherlands. Plies of this fabric are cut from a fabric bobbin into square plies measuring 180mm x
180mm, and stacked in a close fitting mould (see Figure 4.5) up to a maximum depth of 7mm. As with the production of unidirectional composites, the mould is then subjected to heat and pressure.

![Figure 4.5. Schematic of close fitting mould used to consolidate woven fabric plates](image)

Figure 4.5 illustrated that it is possible to produce All-PP composite plates using a range of compaction parameters. To establish the effect of varying compaction pressure on the mechanical properties of All-PP composites, two different techniques are applied to compact the woven composite plates. For pressures in the range 1 – 10 MPa (~10 - 100 bar), a hot press is used.

The composite is placed in a mould, which is positioned between the platens of the hot press. The press used is in this research is a 500kN manual press equipped with electronically controlled heating platens and water-cooled cooling platens. The temperature of the upper and lower heating platens are controlled externally, but the cooling platens are simply cooled by passing cold water through them at mains water pressure and temperature. The cooling platens are fixed between heating platens and the mould to allow rapid cooling of the sample, without having to cool the heating platens. Heating a specimen from room temperature to processing temperature takes approximately 10 minutes while cooling from processing temperature to release temperature (~40°C) is possible in approximately 5 minutes, although these durations are specific to this press and cannot necessarily be scaled up to larger process equipment. During the heating stage of the compaction, the cooling platens and the mould are heated by the heating platens. After the desired compaction temperature has been achieved and held for consolidation, the cooling platens primarily cool the mould since the large volume of the heating platens retains the elevated temperature. Pressure is maintained in the press throughout this process by manual corrections of the applied pressure to balance effects of thermal expansion and contraction caused by heating and cooling of system. The temperature inside the mould is monitored externally using PT100 thermometer probes, inserted in upper and lower halves of the mould, and connected to a PC with data logging software.
Due to the inaccuracy of pressure control of the hot press at very low pressures, specimens compacted at pressures <1MPa (<10bar), are processed by vacuum bagging, rather than hot pressing. To manufacture vacuum bagged specimens, a mould is sealed in a vacuum bag connected to a vacuum pump that applies a negative pressure inside the vacuum bag, and so atmospheric pressure (~0.1MPa) is used to compact the plates (see Figure 4.6). The entire bag is placed inside a circulated hot air oven and consolidation occurs.

Pressure inside the vacuum bag is monitored using a pressure gauge (not shown) outside the oven, connected to the vacuum bag inside. Again, temperature is monitored by two PT100 temperature probes; one is located inside the mould, the other is suspended in the oven to monitor oven air temperature. The specimen is then cooled by removing the vacuum bag from the oven, with the vacuum pump still active; this maintains pressure until the specimen has cooled sufficiently to allow removal of the pressure without risking relaxation of the specimen.

The time-temperature and time-pressure profiles for both methods are shown in Figure 4.7. It is important to note that pressure is applied before heating starts and then remains constant during compaction until the specimen has been cooled to a release temperature (~40°C). The entire cycle from insertion of the mould into the press/vacuum oven until removal of the consolidated plate, has a duration of approximately 30 minutes.

This method maintains a constant compaction pressure to prevent shrinkage during heating and cooling of the composite, and provides consolidation of the tapes when the compaction temperature is reached. Filament wound unidirectional composites and stacked plain woven [0º/90º] ply All-PP composites were made as described for tensile testing. A summary of these and the nomenclature used are shown in table 4.2.
Once compaction temperature is reached in the mould, all the specimens were held for 5 minutes and then rapidly cooled. Compaction pressure was maintained on all specimens during cooling, until 40°C (release temperature) was achieved in the mould. All specimens were cut from these plates by hand, using a razor blade to the dimensions listed in Table 4.3. The dimension of the specimens was limited in some cases by the dimensions of the moulds used to manufacture the specimens. Preliminary experimental work investigated the use of a diamond edged cutting wheel, but this was discontinued due to suspected damage to the specimen. No end tabs were used during testing, as preliminary experiments also showed that the presence of tabs did not influence specimen failure. The specimen edges were sanded after cutting to reduce any edge effects created during cutting. The ‘unidirectional’ samples can be considered slightly off axis due to the winding process, but since the angle of winding is <0.5°, this is ignored.

Table 4.2. Summary of plates created for tensile testing

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tape Geometry</th>
<th>Compaction Temperature</th>
<th>Compaction Pressure</th>
<th>Production Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD140</td>
<td>UD</td>
<td>140°C</td>
<td>2.4MPa</td>
<td>Wound, Hot Press</td>
</tr>
<tr>
<td>UD160</td>
<td>UD</td>
<td>160°C</td>
<td>2.4MPa</td>
<td>Wound, Hot Press</td>
</tr>
<tr>
<td>W140L</td>
<td>Woven</td>
<td>140°C</td>
<td>0.1MPa (Low)</td>
<td>Stacked Plies, Vac. Oven</td>
</tr>
<tr>
<td>W140M</td>
<td>Woven</td>
<td>140°C</td>
<td>1.2MPa (Med.)</td>
<td>Stacked Plies, Hot Press</td>
</tr>
<tr>
<td>W140H</td>
<td>Woven</td>
<td>140°C</td>
<td>12.4MPa (High)</td>
<td>Stacked Plies, Hot Press</td>
</tr>
<tr>
<td>W160L</td>
<td>Woven</td>
<td>160°C</td>
<td>0.1MPa (Low)</td>
<td>Stacked Plies, Vac. Oven</td>
</tr>
<tr>
<td>W160M</td>
<td>Woven</td>
<td>160°C</td>
<td>1.2MPa (Med.)</td>
<td>Stacked Plies, Hot Press</td>
</tr>
<tr>
<td>W160H</td>
<td>Woven</td>
<td>160°C</td>
<td>12.4MPa (High)</td>
<td>Stacked Plies, Hot Press</td>
</tr>
</tbody>
</table>
Table 4.3. Test specimens dimensions

<table>
<thead>
<tr>
<th>Test</th>
<th>Specimens</th>
<th>Tape Orientation</th>
<th>Dimensions*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension</td>
<td>UD140/UD160</td>
<td>0°, 10°</td>
<td>120mm x 12mm x 1mm</td>
</tr>
<tr>
<td>Tension</td>
<td>UD140/UD160</td>
<td>30°, 45°, 60°, 90°</td>
<td>100mm x 25mm x 2mm</td>
</tr>
<tr>
<td>Tension</td>
<td>W140/160/L/M/H</td>
<td>[0°/90°], [10°/80°]</td>
<td>150mm x 12mm x 1mm</td>
</tr>
<tr>
<td>Tension</td>
<td>W140/160/L/M/H</td>
<td>[30°/60°], [±45°]</td>
<td>150mm x 25mm x 1mm</td>
</tr>
<tr>
<td>Compression</td>
<td>UD140C/UD160C</td>
<td>0°, 90°</td>
<td>15mm x 5mm x 5mm</td>
</tr>
<tr>
<td>Compression</td>
<td>W140C/W160C</td>
<td>[0°/90°]</td>
<td>15mm x 5mm x 5mm</td>
</tr>
</tbody>
</table>

(*Dimensions given as length x width x thickness. Exact specimen thickness depends on processing parameters as discussed below)

4.2.2 Tensile and Compressive Testing of Unidirectional and Woven All-PP Composites

Tensile test specimens were tested using an Instron tensile testing machine, equipped with a 5kN load cell and computer running Merlin data acquisition software. Specimens were placed in specially designed composite grips which allow 10° free rotation to reduce the effect of moments in the off-axis specimens. The gauge lengths of unidirectional and woven sample were 120mm and 70mm respectively and tensile tests were performed at 2mm.min⁻¹ with a small preload (~1N). To fully characterise the material, two types of tensile tests were performed: tensile deformation at low strain to determine moduli and Poisson’s ratio, and deformation to failure to determine strength and strain to failure. To determine the Young’s modulus (E-modulus) for each specimen, strain was measured using strain gauges placed in the direction of tensile loading at low strains (<2.5%). The Young’s modulus was calculated in all cases using a range of 0.05% - 0.2% strain; in all cases this proved to be a linear and reproducible region with very little deviation. To determine the Poisson’s ratio, an additional strain gauge was placed at 90° to the direction of loading. To determine the tensile strength and strain to failure of the specimens, high strain (>2.5%) data from the cross-head displacement was used to measure extension. Each test was performed 5 times to ensure reproducibility. Specimens which failed within, or very close to, the gripped region of the specimen were discarded.

Compressive tests, denoted by a ‘C’ suffix in Table 4.3, were performed on specimens manufactured in the same way as tensile specimens, but cut from thicker plates. Compressive tests were performed using a Hounsfield tensile testing machine, configured for compressive loading and equipped with a 2.5kN compression load cell and compression plates (see Figure 4.8). The machine is operated in a tensile mode but the geometry of the compression cell results in a compressive load being applied to the specimen. The specimen geometry is shown in Table 4.3. Tests were performed in accordance with ASTM D695 applying compressive loading at a rate of 1.3mm.min⁻¹. The recorded load increases with compression until ultimately tends reaches a uniform stress. This plateau of constant stress is recorded as the compressive strength. As before, 5 repetitions of each test were performed to provide an accurate measure of the compressive strength. Tests were performed along the longitudinal [0°] and transverse [90°] directions of unidirectional specimens and along one tape direction [0°/90°] of woven tape specimens. All tests reported in this chapter
were performed at room temperature, but the tensile properties of All-PP composites at elevated temperatures have also been investigated but will be presented in Chapter 5.

![Figure 4.8. Schematic of the compression cell](image)

### 4.3 Results and Discussion

#### 4.3.1 Tensile Properties of Unidirectional Composites

The notation used to describe the range of tensile and compressive specimens is described in Table 4.2. Unidirectional specimens (UD140 and UD160) were cut at a range of angles to tape winding direction ($\theta = 0, 10, 30, 45, 60, 90$) from plates manufactured at one of two temperatures: 140°C and 160°C. The tensile moduli and tensile strength of these specimens is presented in Figures 4.9 and 4.10 respectively.

Very little difference was seen in $E_{11}$ between UD140 and UD160, and a greater but still small variation in $E_{22}$. It is clear that unidirectional All-PP composites produced in this way show increased moduli close to the direction of drawing while the transverse modulus is not significantly greater than bulk PP (1-1.5GPa). Figure 4.9 shows the variation of modulus with loading angle for UD160, compared to the model given by equation 4.1. It can be seen there is very small standard deviation and equation 4.1 describes the behaviour of UD160 very well.

Since moduli are very similar for UD140 and UD 160, it suggests that this temperature processing window provides uniform stiffness, and also $E_{11}$ (13±0.8GPa) is 87% ±6% of the modulus of the tape (15GPa) showing a good retention of tape modulus in the composite. Figure 2.27 showed that shrinkage of 1% of a tape led to a decrease in tensile modulus of 22% suggesting that filament
winding is an effective route to prevent relaxation. The off-axis mechanical properties of these unidirectional composites are also shown in Table 4.4.

**Figure 4.9.** Tensile modulus vs. loading angle

**Figure 4.10.** Tensile strength vs. loading angle
Table 4.4. Mechanical properties of unidirectional composite specimens

<table>
<thead>
<tr>
<th>Loading Angle</th>
<th>Compaction Temperature [°C]</th>
<th>Tensile Modulus [GPa]</th>
<th>Tensile Strength [MPa]</th>
<th>Strain to Failure [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Uncompacted Tape</td>
<td>15</td>
<td>450</td>
<td>7</td>
</tr>
<tr>
<td>0</td>
<td>140</td>
<td>13</td>
<td>371</td>
<td>8</td>
</tr>
<tr>
<td>45</td>
<td>140</td>
<td>1.7</td>
<td>8.2</td>
<td>1</td>
</tr>
<tr>
<td>90</td>
<td>140</td>
<td>1</td>
<td>4.5</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>160</td>
<td>13</td>
<td>385</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>160</td>
<td>-</td>
<td>64</td>
<td>2</td>
</tr>
<tr>
<td>30</td>
<td>160</td>
<td>3.5</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>45</td>
<td>160</td>
<td>2.1</td>
<td>8.7</td>
<td>1</td>
</tr>
<tr>
<td>60</td>
<td>160</td>
<td>1.5</td>
<td>6.5</td>
<td>1</td>
</tr>
<tr>
<td>90</td>
<td>160</td>
<td>1.5</td>
<td>4.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Assuming the relationship between tensile modulus and shrinkage is linear in this small region, this decrease in modulus during processing could be caused by relaxation of approximately 0.5% in the length of the wound tape. This is entirely possible due to tightening of the wound tape on the steel frame during processing. Alternatively, relaxation may occur with no decrease in length, if filament winding is perfectly tight, by a chain slipping relaxation mechanism illustrated in Figure 2.28.

The tensile strength as a function of loading angle is shown in Figure 4.10, based on UD140 and UD160. Similarly to off-axis moduli, off-axis strengths, $\sigma_\theta$, are very similar for UD140 and UD160. As discussed in Chapter 2 (see Figure 2.27), this is normal since tensile strength was shown to be much less sensitive to shrinkage than tensile modulus. The shrinkage suggested as the cause for decreased modulus in compacted unidirectional composites would not be seen to affect tensile strength and so this is in agreement with fundamental studies on tape shrinkage. The unidirectional composites are clearly very anisotropic, and while Figure 4.9 shows that while $E_\theta \approx 16\% E_{11}$, $\sigma_{\theta=30} < 5\% \sigma_{11}$. The degree of anisotropy can be described as the ratio of $\sigma_{22}$ to $\sigma_{11}$ and in the case of these All-PP composites, this is 0.011. This is almost three times that seen in unidirectional glass fibre reinforced polypropylene (van der Oever and Peijs, 1998), but this is due to the greater $\sigma_{11}$ value of glass/PP since $\sigma_{22}$ is the same (see Table 4.5).

Table 4.5. Degree of anisotropy of unidirectional All-PP composites compared to unidirectional glass-PP composites (van der Oever and Peijs, 1998)

<table>
<thead>
<tr>
<th>Composite</th>
<th>$\sigma_{11}$</th>
<th>$\sigma_{22}$</th>
<th>$\sigma_{22}/\sigma_{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>All-PP</td>
<td>385</td>
<td>4.5</td>
<td>0.011</td>
</tr>
<tr>
<td>Glass/PP</td>
<td>1025</td>
<td>4.5</td>
<td>0.004</td>
</tr>
</tbody>
</table>

The transition from tensile failure to transverse failure of tapes can be predicted by equations 4.3a-c, and is shown in Figure 4.11. These maximum stress criteria suggest that at $\theta \approx 2^\circ$, failure mode operates via a shearing mechanism and this dominates until $\theta \approx 23^\circ$, and these criteria describe the
experimental data very well, as does the single Tsai-Hill criterion shown in Figure 4.10. The failure of unidirectional specimens is dominated by tape strength at $\theta = 0$, but changes to transverse tape strength as $\theta > 25^\circ$.

Figure 4.11. Tensile strength vs. loading angle with predicted failure mechanism

Figure 4.12 shows a photograph of failed unidirectional specimens tested at $\theta = 0^\circ$, $10^\circ$, $60^\circ$ and $90^\circ$. The specimen loaded at $\theta = 0^\circ$ shows a large amount of fibrillation and no single fracture surface. This is to be expected since the transverse strength of the tapes is so poor that cracks rapidly propagate along the tape direction. It is also clear that a combination of inter-tape debonding and intra-tape fibrillation leads to fibrils being pulled from the composite. This reduces load transfer and it is likely that what is being seen here, is not true tensile failure but instead failure by delamination. This may explain the large difference between the tensile strength of a single tape (450MPa), in which definite tape tensile failure occurs, compared to the tensile strength of a unidirectional composite (380MPa) which shows fibrillation and some fibril pull-out. This is reinforced by Figure 2.27 which shows the stability of tensile strength with small amounts of molecular relaxation. Figure 4.13 shows a composite optical micrograph of a unidirectional All-PP specimen loaded at $\theta = 0^\circ$, in which the complete fibrillation of the composite can be seen.

The specimen tested at $\theta = 10^\circ$ is used to illustrate failure via a shear mechanism. Closer inspection reveals a very small amount of fibrillation at the failure surface, possibly indicating a failure via shear. Specimens loaded at $\theta = 60^\circ$ and $90^\circ$ show clearly that failure has occurred by a transverse failure of the tapes rather than failure of the interface. Figure 4.14 shows the failure surface of a unidirectional specimen loaded at $\theta = 90^\circ$. While the failure surface is not completely flat, the irregularities are clearly much smaller than the tape width (~2mm), indicating that transverse tape failure operates and prevents transverse tape pull out. The fibrillation seen at the failure surface of the specimen tested at $\theta = 90^\circ$ in Figure 4.12 is due to some debonding of surface tapes local to the failure site by peeling rather than transverse tape pullout.
**Figure 4.12.** Photograph of failed unidirectional specimens. (Left to right: $\theta = 0^\circ$, $10^\circ$, $60^\circ$ and $90^\circ$)

**Figure 4.13.** Composite optical micrograph of the fibrillated surface of a unidirectional All-PP composite loaded at $\theta = 0^\circ$
The low transverse strength is partially due to the extremely poor transverse strength of the tape due to high orientation and microvoiding, which limits the transverse composite strength, but also due to the tape geometry. Since the width of the tape is ~36x greater than the thickness of the tape, a large overlap in the transverse direction is present providing excellent load transfer between tapes (Rexer and Anderson, 1979). Thus transverse failure of a unidirectional composite by an interfacial failure mode would theoretically occur by pull-out of the tape width from the surrounding tapes, but this is very unlikely since the transverse strength of the tape is so poor compared to the shear strength of the interface.

The interlaminar shear strength of the composite can be obtained by rearranging equation 4.3b. At \( \theta = 10^\circ \), \( \tau_{12} \) can be predicted since \( \tau_{12} = \sigma_{\theta=10} \)

\[
\frac{\tau_{12}}{\sigma_{11}} \approx 0.171
\]

From Table 4.4, it can be seen that equation 4.6 gives \( \tau_{12} = 65.8 \text{MPa} \). This agrees well with the experimentally determined value for \( \sigma_{\theta=10} \) of 64MPa.

The shear modulus, \( G_{12} \), determined by equation 4.2, has a value of ~0.8GPa for both specimens. Figure 4.15 summarises these mechanical properties as a function of compaction temperature. This shows that increasing the compaction temperature between 140°C and 160°C, has only a small effect on mechanical properties. The transverse modulus and longitudinal strength actually increase slightly with increasing compaction temperature, although the increase in longitudinal strength is within the experimental scatter of the results, and the transverse modulus at either temperature is too small to be of serious interest.
4.3.2 Compressive Properties of Unidirectional and Woven Composites

Figure 4.16 shows the compressive strength of unidirectional composites tested in the longitudinal direction, UD$\sigma_{11C}$, and the transverse direction, UD$\sigma_{22C}$, and of a woven tape composite, W$\sigma_{11C}$, compacted at 140°C and 160°C. There is no increase in the transverse compressive strength of the unidirectional composite but there is a noticeable increase in compressive strength in the longitudinal direction. An increase can also be seen in the compressive strength of the woven composite with increasing compaction temperature.
A photograph of a typical failed woven composite compression specimen is shown in Figure 4.17. In these photos, the dark regions are tapes travelling into/out of the plane of the paper while the light regions are tapes travelling left to right in plane of the paper. The tape structure is clearly buckled, with some interfacial failure in the buckled region.

![Image of composite specimen with failure modes](image)

**Figure 4.17.** (Top) Optical micrograph of a cross-section of a compression testing specimen (W160C) which has failed by buckling, and (bottom) increased magnification of buckled region showing tape buckling and delamination. (Compression loading direction is horizontal)

The increase in compressive strength of the woven tape composite with increasing compaction temperature can be attributed to the increase in interfacial strength with increasing compaction temperature. However, since failure is by buckling, the bending stiffness must also contribute to the compressive strength. The bending stiffness of a woven fabric is mainly due to the bending stiffness
of the tapes in the longitudinal direction, and so the transverse tapes do not contribute greatly to the bending stiffness during buckling. This is supported by considering that the increase of the compressive strength of the woven composite specimen with increasing compaction temperature is approximately half that of the increase of the unidirectional specimen with increasing compaction temperature. This is due to the 50% volume fraction of tapes in the longitudinal direction present providing bending stiffness in the woven tape composite. A higher magnification of Figure 4.17 shows that in the buckled region of the failed specimen, some delamination is seen with some fibrillation traversing the delaminations. It is likely then that the increase in compressive strength with increasing compaction temperature is due to the increase in interfacial strength resulting from higher compaction temperatures.

As described in Chapter 2, the drawing mechanism increases tensile properties by aligning the microstructure of the material in the drawing direction and so it is unlikely that any increase would be seen in compressive properties of tapes. A compressive strength of oriented polypropylene of ~40MPa has been reported for draw ratios \( \leq 5 \), and seem to be independent of draw ratio in this region (Duckett et al., 1972). Failure in these specimens is also by buckling. In fact, failure is reported to occur along shear planes, and so a higher orientation structure may be more susceptible to buckling than an isotropic structure (Shinozaki and Groves, 1973a, b). However, the compressive strength seen here is very close that of bulk PP (~50MPa), and since tensile tests have shown that there is very little affect of processing temperature in this region on the microstructure of the PP tapes, it is likely that no benefit is gained by using this highly oriented PP rather than bulk PP for pure compressive applications.

### 4.3.3 Tensile Properties of Woven Tape Composites

The tensile properties of woven tape composites are presented in Figures 4.18 and 4.19, showing tensile strength and modulus, respectively as a function of loading angle \( \theta = 0, 10, 30, 45 \). From Figure 4.18, the values obtained for processing temperatures of 140°C and 160°C both show very similar strengths but as \( \theta > 0 \), a difference in strength between specimens with these compaction temperatures is observed.

As the processing temperature increases, the off-axis strength of these composites increases. This can be expected because the strength of off-axis composites is due to interfacial bond strength between tapes resisting delamination and so tape pull-out; at \( \theta = 45^\circ \), failure occurs by intraply shearing and tape pull-out. As compaction temperature increases, the interfacial strength increases (see Chapter 3), and so superior load transfer increases the total strength of the composite structure.

Figure 4.20 shows photographs of tensile testing specimens which have failed by a variety of mechanisms. The two specimens on the left of the photograph are \([0^\circ/90^\circ]\) specimens compacted at 140°C and 160°C, and 0.1MPa and 1.2MPa respectively. The main difference between these two specimens is the improved interface as established earlier and this clearly affects the failure mode of these two specimens. Specimen W140L shows large amounts of delamination with entire plies of fabric debonding from the composite together with some small fabric breakage along the length of the composite.
Specimen W160M shows a completely different failure mode; a single failure is seen in the centre of the specimen length with some very localised microfibrillation, but no complete tape pull-out. Since tests on unidirectional specimens showed a negligible decrease in tensile strength of the longitudinal tapes with increasing compaction temperature, this change in failure mode must be due to increased consolidation preventing interlaminar failure and allowing local stresses to build up to reach the longitudinal tensile strength of the tapes.
A similar effect is seen in the case of woven fabric composites tested in the \([\pm 45^\circ]\) direction. Unlike in the case of loading W140M in the \([0^\circ/90^\circ]\) direction, shear deformation over the length of the specimen is clear visible by a reduction in specimen width following loading in the \([\pm 45^\circ]\) direction. This reduction in width is accompanied by an increase in specimen thickness caused by the trellis effect (see Figure 6.16). Figure 4.21 shows composite optical micrographs of the failure surfaces of (a)W140L and (b)W160H. Ultimately, as in the case of \([0^\circ/90^\circ]\) loading, failure of W140L is by a tape pull-out mechanism following rotation of the tapes to align nearer to the loading direction, as can be seen at the failure location. Specimen W160H also shows a high degree of deformation over the whole specimen length due to tape shearing, but in this case, tape pull-out is absent at the failure location. Instead, tape breakage occurs and the failure site is similar in appearance to the failure site of \([0^\circ/90^\circ]\) specimen, with a ‘hairy’ fracture surface showing very localised microfibrillation. In either case, tapes have rotated from \(\pm 45^\circ\) to \(27^\circ\) to the loading direction.

![Figure 4.20. Failure modes of woven tensile specimens](image)

The concept of intraply shearing and fibre pull-out is reinforced by Figure 4.22, which shows the strain to failure of woven tape composites. At \(\theta = 0^\circ - 10^\circ\), the strain to failure is very low, approximating the strain to failure of a single tape, since this failure mode is dominated by tapes loaded in tension. As \(\theta\) increases, increasing amounts of shearing and fibre pull-out lead to a much
greater apparent strain to failure of the composite system of ~40%. The effect of processing parameters is less clear, but specimens compacted at lower temperatures show a greater strain to failure due to the lower interfacial strengths (see Figure 3.25) allowing greater fibre pull-out.

![Composite optical micrographs of failure sites of woven All-PP composites compacted at (a)W140L and (b)W160H loaded at θ=45°](image)

**Figure 4.21.** Composite optical micrographs of failure sites of woven All-PP composites compacted at (a)W140L and (b)W160H loaded at θ=45°

The effect of processing conditions on the off-axis tensile modulus is much smaller. Since the modulus depends on the microstructure of the tapes, whereas the tensile strength depends on the macrostructure of the composite, it has already been shown for a unidirectional specimen that the modulus is largely unaffected by processing temperature within this range. However, increasing the pressure during compaction seems to increase the modulus of a composite at all loading angles. The greatest modulus seen is for the specimen with the greatest applied pressure and temperature, is 53%E₁₁ of the tape, and since the volume fraction of longitudinally oriented tapes in the woven fabric is 50% and the transverse modulus, E₂₂, is very small (see Figure 4.12), this agrees with the rule of mixtures (equation 1.2). Since the greatest value of modulus seen in Figure 4.19 agrees with the rule of mixtures, it would appear that a decrease in properties is seen in composites produced at lower temperature/pressure. The compaction temperature affects the interfacial strengths of All-PP composites and clearly this controls the failure mode of a composite system. Interfacial studies on the fabric showed a small increase in interfacial strength due to increasing the compaction temperature from 140°C to 160°C (see Figure 3.22, fabric A). But
Figures 4.18 and 4.19 showed that the greatest effect on mechanical properties was due to the pressure rather than the temperature applied during compaction of the composites. This observation will now be explained.

It was observed during specimen production that processing temperature and pressure alter the density of the resulting composites. Density tests were performed on samples taken from the same composite plates used for tensile testing, using the Archimedes principle described in Chapter 2. The relationship between the density of the plates and the processing parameters is presented in Figure 4.20. It can be immediately seen that with increasing processing pressure, plate density increases for woven tape plates. The effect of increasing compaction temperature is a positive shift in density. The tape density, $\rho_{\text{tape}}$, is also shown in Figure 4.20, and is less than the density of isotropic polypropylene due to the presence of microvoids as described in Chapter 2. The woven tape specimens, W140 and W160, compacted at 0.1MPa have a density of even less than the original tape. This can only be caused by the presence of interply voids, caused by the surface irregularity of adjacent woven plies, due to tape crimping. In these specimens, consolidation is incomplete and poor interfacial properties would be expected. With increasing compaction pressure, specimens compacted at both temperatures show an increase density, reaching and exceeding original tape density, $\rho_{\text{tape}}$. Thus with increasing pressure, there will be a transition from a combined state of interply and intraply voids, to solely intraply voids. At the highest pressure applied here, 12.4MPa, a density of ~0.87g.cm$^{-3}$ is achieved.

From Figure 4.23, the trends for compaction temperatures of 140°C and 160°C have an approximately constant difference suggesting that the density is predominantly dependant on compaction pressure, rather than temperature. An increased temperature will assist the filling of these voids by reducing the viscosity of the copolymer layer and encouraging flow, but compaction temperature in the range considered is not the dominant parameter. By assuming that filament wound unidirectional composites possess a perfect, void free tape stacking arrangement, the effect of
compaction pressure would not be seen in unidirectional composites. Specimens UD140 and UD160 have very similar density, ~7% greater than that of the tape. The small difference in density between the tape and the unidirectional specimens is probably due some closure of intraply voids during compaction. The presence of interply voids in woven tape fabric must strongly affect the mechanical properties of woven tape composites since the voids can make no load bearing contribution to the composite structure in tension. Since tensile strength and modulus are inversely proportional to the cross-sectional area subjected to loading, the results presented in Figure 4.18 and 4.19 can be reassessed by normalising for variations in density, and are shown in Figures 4.24 and 4.25 respectively.

![Figure 4.23. Effect of processing parameters on plate density](image)

Figures 4.24 and 4.25 present the specific properties of the woven tape plates of the same data, i.e. normalised for the measured composite density. The general behaviour of these curves is similar to Figures 4.18 and 4.19, but the magnitudes of the strengths and moduli become closer, and are less directly linked to processing parameters. As in Figures 4.18 and 4.19, the optimum performing plates are those with highest processing temperature and pressure. This suggests that providing that molecular relaxation is prevented, tensile properties of All-PP composites increase with increasing compaction pressure and temperature. The specific mechanical properties in the [0°/90°] direction as a function of compaction pressure are shown in Figure 4.26.

Figure 4.26 further reinforces the concept that mechanical properties are not very sensitive to changes in compaction temperature in the range 140°C~160°C. It is likely that a set of optimum compaction conditions will be seen with increasing compaction temperature and pressure, but ultimately these will encourage plastic flow, allowing molecular mobility and a loss of mechanical properties. To fully understand the changes in density seen in these composite plates, cross sections of woven tape composite plates were viewed using optical microscopy. These images are presented in Figure 4.27. Although some degree of crimping is seen in the compacted tape, the degree of crimping is reduced by the use of a thin tape geometry reinforcement, rather than a traditional cylindrical fibre such as glass, which typically leads to a much higher degree of crimping.
In Figure 4.27, light and dark areas are clearly visible in the composite cross sections. The light areas are tapes travelling along the width of the specimen from left to right on the page. The dark areas are tapes travelling out of the plane of the page. The increase in compaction temperature from 140°C (left hand side) to 160°C (right hand side) shows little change, but increasing pressure (top to bottom of page) has a noticeable affect. Even though all cross sections are presented at the same scale, the increase in density is clearly seen as the thickness of the plates decreases noticeably with increasing pressure. Also seen in specimens compacted at 0.1MPa is the conspicuous presence of
interply voids, proving their existence. These interply voids are also seen in specimens compacted at 1.2MPa at both temperatures but are absent from those compacted at 12.4MPa and 160°C. Therefore it would seem that the optimum pressure to eliminate these interply voids is between 1.2MPa and 12.4MPa, but also the exact value of this ‘optimum’ pressure may depend on compaction temperature since following compaction at 140°C, even 12.4MPa is insufficient to totally close all the interply voids. This means that even though Figure 4.22 showed that the composite plates processed at 140° and 160°C, exceed the density of the tape when compacted at 0.35MPa and 1.85MPa respectively, Figure 4.27 shows that interply voids are still present in composites. The composite processed at 140°C and 12.4MPa has a density of ~0.83g.cm⁻³, and so the presence of voids means that the density of the tape must be above this value; intraply voids must be closing before complete closure of interply voids. This complicates a direct comparison between specific modulus of tapes and specific modulus of composites.

Figure 4.26. Specific tensile properties vs. compaction pressure

The total closure of the intraply voids requires an excess of molten copolymer to flow out from between adjacent tapes into the voids. If compaction temperature is too low, the viscosity of the copolymer melt may not be low enough to enable flow into these voids. In this case the voids will remain. The specimen compacted at 160°C and 12.4MPa shows total closure, but in filling the voids, the tapes are forced out of alignment and so more severe crimping is seen in these specimens. This crimping should definitely reduce the performance of the composite especially in view of the extremely poor off-axis properties of the tape. However, even though the degree of crimping is more severe, greater consolidation results in greater alignment of the longitudinal tapes since the composite thickness decreases with increasing consolidation.
Figure 4.27. Cross-sections of woven tape composites compacted with increasing temperature and pressure.
4.4 Conclusions

It has been shown in this chapter that the parameters applied to consolidate All-PP composite specimens determine the mechanical properties. Despite the high temperatures involved during the compaction process, the high strength and stiffness of a highly oriented polymer tape can be retained in a composite laminate. Furthermore, the composite is not sensitive to deviations in process temperature since mechanical properties proved approximately constant within the temperature processing window applied (140°C - 160°C).

The original reason for applying pressure during the compaction of woven tape All-PP composites was to prevent shrinkage and relaxation by lateral constraining. Subsequently it became obvious that pressure was also required to provide good surface contact by making the opposing surfaces, which maybe uneven due to tape weave, meet.

The compaction temperature and pressure can affect the mechanical properties of these composites by altering both the mesostructure of the composite (i.e. the structural composition), and the microstructure (i.e. the molecular orientation) of the tape material, but by choosing suitable parameters, loss of mechanical properties can be minimised. This study has clarified the relationship between these parameters and the mechanical performance of the composite although further study may reveal absolute optimum processing conditions.

A summary of the mechanical properties for unidirectional and woven tape fabric plates are presented in Table 4.6 and 4.7 respectively.
### Table 4.6. Mechanical properties of unidirectional specimens

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>140°C</th>
<th>160°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure [MPa]</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Density, [g.cm⁻³]</td>
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<td>0.77</td>
</tr>
<tr>
<td>E₁₁, [GPa]</td>
<td>12.93</td>
<td>12.95</td>
</tr>
<tr>
<td>E₁₁/ρ [GPa.g⁻¹.cm³]</td>
<td>16.79</td>
<td>16.82</td>
</tr>
<tr>
<td>E₂₂ [GPa]</td>
<td>0.91</td>
<td>1.52</td>
</tr>
<tr>
<td>E₂₂/ρ [GPa.g⁻¹.cm³]</td>
<td>1.18</td>
<td>1.97</td>
</tr>
<tr>
<td>σ₁₁ [MPa]</td>
<td>371</td>
<td>385</td>
</tr>
<tr>
<td>σ₁₁/ρ [MPa.g⁻¹.cm³]</td>
<td>482</td>
<td>500</td>
</tr>
<tr>
<td>σ₂₂ [MPa]</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>σ₂₂/ρ [MPa.g⁻¹.cm³]</td>
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<td>5.84</td>
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<td>σ₁₁C [MPa]</td>
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<td>55.8</td>
</tr>
<tr>
<td>ν₁₂</td>
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<td>0.38</td>
</tr>
<tr>
<td>ν₂₁</td>
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<td>0.06</td>
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<tr>
<td>G₁₂ [GPa]</td>
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</table>

### Table 4.7. Mechanical properties of woven specimens

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<th>Temperature [°C]</th>
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<th>160°C</th>
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</thead>
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<td>Pressure [MPa]</td>
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<td>1.2</td>
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<td>Density, [g.cm⁻³]</td>
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<td>5.53</td>
</tr>
<tr>
<td>E₁₁/ρ [GPa.g⁻¹.cm³]</td>
<td>5.85</td>
<td>7.90</td>
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<tr>
<td>E₄₅ [GPa]</td>
<td>1.88</td>
<td>2.28</td>
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<td>E₄₅/ρ [GPa.g⁻¹.cm³]</td>
<td>2.94</td>
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<td>σ₁₁ [MPa]</td>
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<td>181</td>
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<td>σ₁₁/ρ [MPa.g⁻¹.cm³]</td>
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</tr>
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<td>σ₁₁C [MPa]</td>
<td>-34.4</td>
<td>-</td>
</tr>
<tr>
<td>ν₁₂</td>
<td>-0.07</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Chapter 5

Time-Temperature Dependent Properties of All-PP Composites

5.1 Introduction

In Chapter 4 of this thesis, the tensile and compressive properties of woven All-PP composites were determined by static tensile tests at room temperature. However, since the mechanical properties of polymers are totally dependant on intermolecular interactions, the performance of polymers depends on the applied strain rate and temperature of loading. For amorphous polymers, the effect of temperature and duration of loading can be equivalent. For example, loading an amorphous polymer at a high strain rate can be equivalent to loading at a low temperature and vice versa. Thermal transitions are seen in which a dramatic change in mechanical properties (e.g. stiffness) can be seen over a small range of temperatures. These transitions are caused by conformational changes becoming possible due to increased thermal energy in the system. An example of such a thermal transition is the glass transition temperature, at which temperature large segmental chain motion becomes possible leading to a large decrease in the stiffness of amorphous polymers. The behaviour of a semi-crystalline polymer such as polypropylene is much more complex since not only does the crystalline phase exhibit thermal transitions in addition to the thermal transitions normally seen in the amorphous polymers, the crystal phase also imposes restrictions on the mobility of the amorphous phase. This complicates the prediction of the behaviour of semi-crystalline polymers at elevated or reduced temperatures.

5.1.1 Time Temperature Superposition

Experimental data determining the dynamic response of a polymer loaded at different strain rates is limited by the range of strain rates which can be applied for a particular test method. It is often desirable to obtain information about strain rates outside the range that can be achieved experimentally, in order to predict the behaviour of materials over very long loading times. The behaviour of amorphous polymers during deformation can be described by considering deformation as a series of conformational changes of the polymer molecules. In order for these small changes in
molecular conformation to occur, an energy barrier must be overcome. This is achieved via random molecular vibrations due to thermal energy. Since the thermal energy in a system is statistically distributed, the probability of a change in conformation occurring increases with time. This probability increases dramatically with increasing temperature, and so for a change in conformation, a characteristic transitional temperature is seen at which a significant number of confirmation changes occur. Thus in a fixed time scale $t_s$ the temperature required to achieve a certain change in conformation can be defined as

$$
t_s = A e^{\left(\frac{E_a}{kT}\right)}
$$

This gives

$$\ln t_s = c + \frac{E_a}{kT}
$$

Where $t_s =$ Time scale

$A, k, c =$ Constants

$E_a =$ Activation energy of the change in conformation

$T =$ Temperature

Thus time and temperature can be considered equivalent during the deformation of amorphous polymers since conformational changes are aided by thermal energy. These changes can occur very rapidly at higher temperatures, but can equally occur at lower temperatures over larger time scales. This is important as the principle of time temperature superposition states that it is possible to provide information on strain rates outside the range experimentally available, by shifting data obtained experimentally by a shift factor $aT$ in the time scale. Practically, data is obtained at the widest range of strain rates experimentally possible, at a range of temperatures. This data can then be shifted by $aT$ to higher or lower time scales since these are equivalent at higher or lower temperatures; lower temperature experimental data provides information about shorter loading rates and vice versa. This shift factor can be modelled using an Arrhenius equation. The result of shifting data in this way is a ‘mastercurve’ of data which provides a much wider range of information than experimentally possible for a given reference temperature, $T_{ref}$.

In order to use mastercurves to predict the long term behaviour of polymers, the polymer must show a constant temperature dependence and a constant thermal activation energy, $E_a$. While the prediction of mechanical behaviour of amorphous polymers is possible, it grossly oversimplifies the complex behaviour seen in semi-crystalline polymers which may possess a combination of thermal transitions and an irregular temperature dependence. If a polymer shows a single change in conformation, the characteristic time scale will have a constant temperature dependence, and the polymer can be described as being thermo-rheologically simple (see Figure 5.1).

However, polymers often show multiple changes in conformation, and each transition time scale may possess a different temperature dependence. In this case, the polymer is described as being thermo-rheologically complex, and the dynamic mechanical behaviour cannot be predicted by solely shifting in the time scale (see Figure 5.2) (Klompen, 1996). It is clear that the transition times of processes at two temperatures, $T_1$ and $T_2$, in Figure 5.2 cannot be shifted solely by a single
horizontal ($a_T$) shift, since two component thermal effects are present with different shift factors, $a_{T1}$ and $a_{T2}$. It is possible to create mastercurves of thermo-rheologically complex polymers by combining a single horizontal shift factor, $a_T$, with a vertical shift factor, $\beta_T$, although this is outside the scope of this thesis (Boyd, 1984).

**Figure 5.1.** The temperature dependence of the conformation transition time of a thermo-rheologically simple polymer

![Figure 5.1. The temperature dependence of the conformation transition time of a thermo-rheologically simple polymer](image1)

**Figure 5.2.** The temperature dependence of the conformation transition time of a thermo-rheologically complex polymer

![Figure 5.2. The temperature dependence of the conformation transition time of a thermo-rheologically complex polymer](image2)
In the case of a thermo-rheologically simple material, the shift factor, $a_T$, can be given by equation 5.3.

$$\log a_T = \frac{E_a}{2.303 R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)$$  \hspace{1cm} 5.3

Where

- $a_T$ = Shift factor
- $E_a$ = Activation energy for the change in property
- $R$ = Universal gas constant [8.314 J.mol$^{-1}$.K$^{-1}$]
- $T$ = Absolute temperature of data to be shifted
- $T_{ref}$ = Absolute reference temperature of data

Using this shift factor, it is possible to create a mastercurve to predict the mechanical behaviour over a much wider range of strain rates at a single reference temperature, $T_{ref}$. The use of these techniques assumes time and temperature equivalence and does not include any allowance for degradation or aging of the polymer due to environmental effects, which would occur due to actual loading at large time scales. The aim of this chapter is to investigate the response of All-PP composites to tensile and flexural loading at a wide range of temperatures and strain rates. By characterising this response, mastercurves will be created in order to assess the performance of All-PP composites at strain rates outside those achievable in the laboratory.

5.2 Experimental Procedure

5.2.1 DMTA of Single Tapes

Dynamic mechanical thermal analyses (DMTA) were performed on co-extruded PP tapes as described in section 2.2, with draw ratio, $\lambda$=4, 6, 12 and 17. Specimens were tested in a TA Instruments DMAQ800 DMTA machine fitted with tensile testing head. A gauge length of 10mm was used, and since all tapes were drawn from the same original co-extruded tape, thickness and width of tape depend on draw ratio. The system was automatically cooled to below -50°C, and then heated at a rate of 1°C.minute$^{-1}$ to 160°C. A static force of 10mN was applied to ensure that the tape was taut between the tensile grips. The force was kept constant during testing to allow shrinkage of the tape during testing.

5.2.2 DMTA of Woven Tape Composites

Dynamic mechanical thermal analyses were performed on woven tape All-PP composite plates manufactured as described in section 4.3.1. The plates were produced at compaction temperatures of 125°C, 140°C and 160°C, and at a pressure of 4MPa. Specimens were cut from this plate with dimensions of approximately 30mm x 8mm x 1mm either 0°/90° to the tape direction or ±45° to the tape direction. These specimens were tested in a Rheometric Scientific Mk II DMTA machine fitted with a dual cantilever bending test assembly and data acquisition software. The specimens were placed in the test grips inside a heating chamber and then the specimen and grips were cooled to below -80°C, by the manual addition of liquid nitrogen to the chamber. At this point, the chamber
was removed and the grips were retightened to a torque of 10cN.m, and the chamber was replaced and recooled to below -80°C. When the temperature inside the chamber fell to below -80°C, the chamber was heated at a rate of 1°C.minute⁻¹, and when the chamber rose to -80°C, the specimen was subjected to a sinusoidal flexural displacement applying a maximum tensile strain of 0.2% at frequencies of 100Hz, 10Hz, 1Hz and 0.1Hz. For each frequency, the storage modulus and the loss factor were recorded. The data acquisition at this heating rate provided data points at a rate of approximately 1 measurement per frequency per 2 minute interval. The chamber was heated to 170°C at this rate, although useful data above 165°C was not achieved due to relaxation and shrinkage of the test specimen.

5.2.3 HDT Simulation

The heat deflection temperature (HDT) test is an industry standard with little scientific value, used as a simple comparison of the thermal flexural stability of materials. The test is described fully in ASTM D648. The HDT test yields a single temperature value at which a mid-span deflection of 0.25mm is attained, due to a static flexural load applied to the test specimen during exposure to increasing temperature at rate of 2°C.minute⁻¹. The two standard loads used are 0.455MPa and 1.82MPa; only 1.82MPa is considered in this research. Since this test specifies a flexural deformation and specifies specimen dimensions, a flexural strain is also specified:

\[ r = \frac{6dD}{L^2} \]

Where  
\( r \) = strain of outermost fibres  
\( d \) = midspan deflection  
\( D \) = specimen thickness  
\( L \) = span length

For the HDT test in ASTM D648, \( d = 0.25\text{mm} \), \( D = 13\text{mm} \), and \( L = 100\text{mm} \), giving \( r = 0.195\% \). Therefore, the HDT test can be interpreted to specify the temperature at which a certain strain is achieved. Moreover, since the applied stress is constant, the HDT temperature can be considered to specify the temperature at which a certain effective flexural modulus is achieved. Flexural stress is constant at 1.82MPa, so this test specifies the temperature at which a flexural modulus of 0.933GPa is reached. The test involves the static loading of a body so relaxation processes may operate, but if these are ignored, the HDT test can be compared to DMTA of plates, as described above, in which flexural dynamic moduli are measured as a function of increasing temperature.

5.2.4 Static Tensile Testing at Elevated Temperatures

Static tensile tests were performed on woven tape composite plates at a range of discrete temperatures in the range -40°C to 150°C using the same tensile testing equipment described in section 4.3.2. The plates used for this research were compacted at a temperature of 140°C and a pressure of 4MPa. To achieve this range of temperature, an Instron 3119 environmental chamber was fitted to the testing machine as shown in Figure 2.13. This chamber allows heating via a circulating air oven and cooling via a liquid nitrogen supply. A gauge length of 70mm and a
crosshead displacement speed of 5mm.minute$^{-1}$ were used. The specimens were fitted between tensile testing grips at room temperature and then the chamber was cooled/heated to testing temperature. The temperature was held for 5 minutes to allow uniform temperature within the specimen, and then tensile testing was commenced. If reduced temperatures were applied, tensile grips were retightened at reduced temperature prior to holding since thermal contraction leads to loosening of the specimen in the grips. For each temperature, two sets of experiments were performed. Firstly, the tensile moduli were determined by using a thermally stable clip-on extensometer and a strain range of 0-0.2%. The tensile strengths and strains to failure were determined by loading the specimens to tensile failure. Since there is a risk of damage to the extensometer during tensile failure, it was preferable to use different specimens for modulus and strength measurements.

5.2.5 Reference Materials

In addition to PP tapes and All-PP composites used in this chapter, two types of glass reinforced PP are used for comparison. The first is Symalite® (hereafter referred to as GMT) manufactured by Quadrant Composites, and is a random, discontinuous glass reinforced PP with a fibre weight fraction of 23% and was supplied in 4mm thick sheets. The second, Twintex®, produced by Saint Gobain-Vetrotex, is a balanced, woven glass reinforced PP with a fibre weight fraction of 40% and supplied in 2.3mm thick sheets.

5.3 Results and Discussion

5.3.1 Dynamic Thermal Mechanical Properties of Single Tape

The effect of temperature on the dynamic storage modulus, $E'$, of a range of tapes with increasing draw ratio at a frequency of 1Hz is shown in Figure 5.3. Also shown on Figure 5.3 is the storage modulus of an isotropic PP specimen (PP homopolymer H4, as described in Table 2.4). The storage modulus of these tapes clearly decreases with increasing temperature as would be expected of a semi-crystalline polymer. All the tapes show a similarly shaped curve to the undrawn specimen and for all the drawn tapes, the storage modulus increases with increasing draw ratio.

Figure 5.4 shows this data as a function of draw ratio. As with tensile modulus at room temperature (see Figure 2.19), storage modulus at room temperature increases almost linearly with draw ratio. At -50°C, the storage modulus is shifted vertically by 4GPa±0.8, compared to the storage modulus at 20°C. At 120°C, lower draw ratio tapes, $\lambda=4$ and 6, possess the same storage modulus, approximately 0.2GPa, as undrawn PP. This suggests that the tapes have totally relaxed and reflects the lower thermal stability of these low draw ratio tapes as was presented in Chapter 2 of this thesis.

The higher draw ratio tapes, $\lambda=12$ and 17, retain a higher modulus at elevated temperatures, possessing storage moduli of 1.3GPa and 3.3GPa respectively at 120°C. These values are similar to those reported for PP oriented to similar draw ratios by roll drawing (Taraiya et al., 1987; Yang et al., 1994) and hot air drawing (Unwin et al., 1990). This data shows that the storage modulus of a tape drawn to $\lambda=17$, still possesses a greater storage modulus at 120°C than undrawn PP possesses at room temperature.
Figure 5.3. Storage modulus vs. temperature for a range of PP tapes with increasing draw ratio.

Figure 5.4. Storage modulus vs. draw ratio for a range of PP tapes with increasing test temperature.

Figure 5.5 shows the variation of loss factor, \(\tan \delta\), with temperature for tapes with draw ratios, \(\lambda = 1\) (undrawn), 4, 6, 12 and 17. Firstly, a decrease in sub \(T_g\) \(\tan \delta\) is seen with increasing \(\lambda\). This is explained by the increasing orientation (and so order) of interlamellar amorphous PP, with increasing draw ratio (Gibson et al., 1978). A similar trend in loss factor was also reported for hydrostatically extruded LPE (Gibson et al., 1982), with the loss factor decreasing with increasing draw ratio, \(\lambda\).
In Figure 5.5, the undrawn specimen shows a peak in tan \( \delta \) at approximately 0°C. This is associated with the glass transition temperature, \( T_g \), (\( \beta \) relaxation) of isotactic PP, although it is not possible to exactly define the \( T_g \) from this graph since the peak is rather broad. A similar peak is seen in the tape drawn to \( \lambda = 4 \), although the peak is shifted to a slightly higher temperature, and the height of the peak is reduced. There is a suggestion of a peak in tan \( \delta \) for the tape drawn to \( \lambda = 6 \), but much reduced in magnitude.

Since this tan \( \delta \) peak is associated with \( T_g \), it is reasonable to expect a reduced effect of \( T_g \) for tapes with higher draw ratio, as with increasing draw ratio the amorphous phase of PP becomes oriented along the drawing direction (Jawad and Alhaj-Mohammad, 1994). The amorphous phase becomes tightly stretched between crystalline regions forming taut tie molecules, and so has less freedom to engage in small conformational changes (Taraiya et al., 1987). Therefore, in highly oriented PP systems, the glass transition normally seen in isotropic PP is greatly reduced. This can also be seen in Figure 5.3, in which no significant decrease in storage modulus is seen around the normal glass transition temperature of PP. The highly oriented amorphous phase can be given sufficient energy to allow these conformational changes to occur, but at increased temperatures compared to unoriented PP. This is reflected in the slight increase of \( T_g \) with \( \lambda \). The transition is likely to be shifted to higher temperatures. From Figure 5.3 the most noticeable decrease in the tape drawn to \( \lambda = 17 \) is at 50°C, and this could account for a glass transition effect which has been shifted to higher temperatures by the high degree of orientation of the amorphous phase.

Figure 5.5 shows that another transition, \( T_{\alpha} \), is seen at higher temperatures and at first glance has an unclear relation with \( \lambda \). However, on closer analysis this trend is the same as that seen for tape shrinkage (see Figure 2.24). An increase in draw ratio to \( \lambda = 9 \) encourages shrinking on heating by only slightly deforming the amorphous phase, which can easily contract on heating to pull the crystalline regions closer together.
Thus at $\lambda \leq 9$, a large effect of this transition would be expected and a peak in $\tan \delta$ for tape drawn to $\lambda = 4$, and a larger peak for tape drawn to $\lambda = 6$ are seen in Figure 5.5. A possible explanation can be presented. Since $\alpha$ relaxation is due to a shift in crystal defects (Boyd, 1985; Hu and Schmidt-Rohr, 1999), these conformational changes result in a translation of crystalline molecules normal to the plane of the lamella sheets (Seguela et al., 1999). This translation can cause a loosening of taut tie molecules (see Figure 2.28) which allows relaxation and disrupts load transfer between crystals. The greater crystal continuity achieved by high draw ratios seems to result in a higher temperature requirement for this transition to occur. As draw ratio increases from $\lambda = 4$ to 6, the magnitude of the peak in $\tan \delta$ becomes larger since the greater deformation achieved by drawing leads to greater numbers of oriented tie molecules. However, as $\lambda$ reaches 12 and 17, the tapes become more thermally stable due to the drawn structure, and the greater crystal continuity requires greater thermal energy to allow conformational changes (Roy et al., 1988).

### 5.3.2 Dynamic Thermal Mechanical Properties of Woven Tape Composites

Woven tape All-PP composites have been made from the same $\lambda = 17$ tape described above. When tested in dual cantilever bending mode along one tape direction, these composites show a similar dynamic response to individual tapes. Figure 5.6 shows the storage modulus of 3 All-PP composite plates and a plate of undrawn PP, as a function of temperature. The three All-PP composites specimens used are compacted at $125^\circ C$, 140$^\circ C$ and 160$^\circ C$, respectively, to investigate any effect of this compaction temperature on dynamic thermal mechanical properties.

As with the static modulus (see Figure 4.17), there is a slight increase in dynamic storage modulus with increasing compaction temperature. The difference between these specimens becomes greater at lower temperatures, so that at -80$^\circ C$, the specimens compacted at 160$^\circ C$ have a 20% greater
storage modulus than those compacted at 125°C. All the specimens have a similar decrease in storage modulus between room temperature and 100°C. An interesting effect is witnessed at temperatures above 100°C. There is a small but consistent decrease in storage modulus which occurs at approximately the same temperature as the compaction temperature of the specimens. To illustrate this point, data in this region from Figure 5.6 is shown in more detail in Figure 5.7.

![Figure 5.7. Detail of Figure 5.6 at a higher temperature range](image)

The effect in the specimen compacted at 160°C is most pronounced. Since the effect is smallest for the specimen compacted at 125°C, it is unlikely this will affect the use of the composites as application in this temperature range is not envisaged, due to the thermal shrinkage that may occur. If this effect can be attributed to the compaction temperature it may be of prime interest if further development of these All-PP composites involves co-extruding with a lower melting temperature copolymer. Lower compaction temperatures would result in sufficient consolidation, but this effect may reduce high temperature performance of the composite, although this effect seems to decrease with decreasing compaction temperature. Since this effect is very small it does not drastically affect composite performance and it requires further investigation to determine the exact mechanism.

Specimens cut from the same composite plate show exactly the same behaviour when tested at 45° to the tape direction (see Figure 5.8). Since loading is not transferred along the tape direction, the storage modulus is lower than for 0°/90° specimens. The proportional difference between composites tested at 0°/90° to tape direction and ±45° to tape direction is approximately 45% and is the same as the difference seen in static tensile testing of these composites (see Figure 4.17). As before, the decrease in storage modulus is seen at the compaction temperature. The loss factor for 0°/90° and ±45° specimens were identical and the loss factor as a function of temperature for All-PP composites compared to undrawn PP, is shown in Figure 5.9.
The trend is the same as seen in Figure 5.5; the tapes present in the composite are drawn to $\lambda=17$. A clear peak in tan $\delta$ attributable to glass transition is not visible in Figure 5.9. A more definite peak is seen in tan $\delta$ corresponding to $T_\alpha$. The magnitude of this peak increases with increasing compaction temperature. It has been reported that the $\alpha$ transition decreases with increasing draw ratio in highly drawn fibres, but reappears in the fibres following annealing (Takayanagi et al., 1966; Owen and Ward, 1973). Since the highly oriented All-PP tapes are effectively being annealed...
during compaction of the fabric into a composite plate, this explains the increasing $\alpha$ transition peak in tan $\delta$ with increasing compaction (annealing) temperature (Nagou and Azuma, 1979; Nagou and Oba, 1980a, b). The presence of this increasing loss factor with increasing compaction temperature, explains the increasing drop in $E'$ seen in Figures 5.6 and 5.8, and the apparently inferior dynamic storage moduli of All-PP plates compacted at increasing compaction temperature, when tested between 60°C and 140°C.

![Figure 5.10. Storage modulus vs. temperature for an All-PP composite, isotropic PP, woven glass PP and GMT (All-PP and woven glass PP tested at 0°90° to tape/fibre direction)](image)

Having established the effect of temperature on the storage modulus of All-PP composites, a heat deflection temperature can be simulated, as described in section 5.3.3. The storage modulus value which simulates the HDT at a load of 1.82MPa is shown in Figure 5.10. The values for GMT here compare very well with those reported in literature (Schledjewski and Karger-Kocsis, 1994). The HDT values are presented in Table 5.1, which compares this method with manufacturers data obtained using standard HDT test equipment, and shows that HDT simulation provides a good correlation in each case. It must be emphasised that the estimation of HDT by DMTA is a simulation and does not account for thermal relaxation of the specimen which may occur in static HDT testing but not in the DMTA simulation. This means that DMTA should overestimate the HDT, due to the absence of creep in the dynamic method. However, the HDTs obtained for both the GMT and woven glass PP represent a flexural deformation near the melting point of PP so a total collapse of the specimen would be expected at these temperatures. By drawing polypropylene, it is clear that the HDT is greatly improved, giving All-PP composites a HDT of only 13% less than GMT.
Table 5.1. Table of HDT and simulated HDT results

<table>
<thead>
<tr>
<th>Material</th>
<th>HDT Simulation (DMTA) [°C]</th>
<th>HDT (ASTM D648) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woven Glass PP (40% wt)</td>
<td>158.6</td>
<td>159 (Twintex, 2003)</td>
</tr>
<tr>
<td>GMT (23% wt)</td>
<td>154</td>
<td>155 (Quadrant, 2003)</td>
</tr>
<tr>
<td>All-PP Composite</td>
<td>134</td>
<td>-</td>
</tr>
<tr>
<td>Undrawn PP</td>
<td>36</td>
<td>-</td>
</tr>
</tbody>
</table>

5.3.3 Static Mechanical Properties of Woven Tape Composites at Elevated Temperatures

To further clarify the static properties of All-PP composites at elevated temperatures, tensile tests were performed on woven tape All-PP composite tensile specimens. The modulus of All-PP composites loaded along the 0°/90° tape direction at a range of temperatures is shown in Figure 5.11, compared to GMT. The comparison with GMT is important as the reinforcing component of GMT, i.e. glass fibres, is not affected by temperature, and so for comparison it is important to know how these composites behave at elevated temperatures.

![Figure 5.11. The tensile modulus of All-PP composites and GMT vs. temperature](image)

These results show similar trends to those obtained by DMTA, although the modulus of All-PP is slightly lower than the GMT at temperatures above 50°C and higher below 50°C, unlike the DMTA results, in which the two materials have similar storage moduli between 20°C and 80°C, and outside this region, GMT has a higher storage modulus than the All-PP composite. The approximately linear behaviour of the tensile modulus of GMT with increasing temperature (between 20°C and...
120°C) has previously been reported (Schledzewski and Karger-Kocsis, 1994), although a decrease in dynamic modulus at $T_g$ is also reported but a decrease in tensile modulus is not clearly visible in Figure 5.11.

![Figure 5.12. The tensile strength of All-PP composites and GMT vs. temperature](image)

The strength of these composites at elevated temperatures also provides useful data on the possible application temperature of All-PP composites. This information is shown in Figure 5.12. With increasing testing temperature, the strength of both the All-PP and the GMT decreases; the decrease in strength of the All-PP composite can be seen to decrease in two linear regions, with a transition at approximately 90°C, which coincides with $T_\alpha$. Since $\alpha$ transitions are associated with increased molecular mobility within the crystalline phase the shear strength of crystals is reduced, and this rapid decrease in strength above $T_\alpha$ may be expected (Wills et al., 1980).

The work to fracture has also been measured from these specimens and is presented in Figure 5.13. The work to fracture during tensile failure is approximately constant up to approximately 90°C, since the same failure modes of tape breakage and delamination operate. As $T_\alpha$ is reached, there is a sudden increase in toughness due to greater strain to failure of the composite. This may be attributed to increased mobility within the crystals allowing the tape to yield more easily in tension, so encouraging greater deformation before failure. This suggests that while the modulus is controlled by a contribution of highly oriented amorphous phase with the crystalline phase, the tensile strength is mainly due to the crystalline phase. Hence, no effect of $T_g$ (amorphous $\beta$ transition) is seen on the tensile strength of the All-PP composites, but an effect due to $T_\alpha$ (crystalline $\alpha$ transition) is clearly visible.
5.3.4 Time Temperature Superposition of Dynamic Modulus and Static Strength Data of Woven Tape Composites

Using the principle of time temperature superposition, this data can be adapted to provide the storage modulus at a wider range of strain rates. Figure 5.14 shows the variation of storage modulus for a range of temperature between -20°C and 70°C, tested at strain rates of 100Hz, 10Hz, 1Hz and 0.1Hz. Using a horizontal shift factor $a_T$, these can be shifted to create a mastercurve at a reference temperature of 20°C. Figure 5.15 shows the dynamic modulus mastercurve.

A similar process can be used to create a tensile strength mastercurve. Tensile tests are performed as before, but at a 3 decade range of strain rates. These can be combined to provide a mastercurve, expanding the strain rate range. In this case, a different shift factor is required. Figure 5.16 shows the tensile strength of the All-PP composite as a function of strain rate at a range of temperatures. By applying a shift factor described by equation 5.4, a strength mastercurve can be created and is shown in Figure 5.17. The shift factors used in Figures 5.15 and 5.17 are shown in Figure 5.18. The activation energy $E_a$ can be determined from equation 5.5, based on equation 5.2.

$$E_a = m(2.303R)$$  \hspace{1cm} \text{5.5}

Where $m$ = Gradient of fit line in Figure 5.18

$R$ = Universal gas constant

Both shift factors show approximately constant values (as indicated by the $r^2$ fit parameter) with an activation energy of $\sim 300\text{kJ.mol}^{-1}$ and $\sim 100\text{kJ.mol}^{-1}$ for dynamic flexural modulus and static tensile strength respectively.
An activation energy of 300kJ.mol\(^{-1}\) is used to shift the modulus mastercurve, which is of the same order as previously reported using the same simple Arrhenius shifting of PP: 210kJ.mol\(^{-1}\) (Faucher, 1959), and 364kJ.mol\(^{-1}\) (Amash and Zugenmaier, 1996) but these are one order of magnitude greater than activation energies used in more complex models of PP, typically 50kJ.mol\(^{-1}\) (Tanner, 1985; Wortmann and Schulz, 1995b, 1996).
This more complex model of Wortmann and Schulz considers the contribution of the temperature
dependence of an elastic and viscous component separately, each with different mechanical
response. Although Arrhenius shifting has been shown to be empirically successful, the validity of
time temperature superposition of PP as a thermo-rheologically simple material has been queried
(Wortmann and Schulz, 1995a). It has been previously reported that using a simple Arrhenius shift can yield unrealistically high activation energies (Fytas and Ngai, 1988).

\[
\text{Figure 5.18. Determination of activation energy for time temperature superposition of tensile strength and dynamic modulus}
\]

Since a single activation energy leads to a good fit of the modulus data it is likely that the same mechanisms are occurring across the strain rate range, which is likely since the temperature range here is quite small. It is likely that this ‘activation energy’ describes a complex series of effects since simple time-temperature superposition is only directly applicable to amorphous polymers. The mastercurve provides useful information about the modulus over loading times from \(10^9\) to \(10^9\) seconds. These are presented as more familiar time equivalents in Table 5.2. However, it must be stressed that these mastercurves provide a prediction of behaviour that is probably quite valid over relatively short time scales i.e. <\(10^6\) seconds, but it is likely that significant deviation is seen at greater time scales.

\[
\begin{array}{|c|c|}
\hline
\text{Time [s]} & \text{Equivalent} \\
\hline
1.58 \times 10^8 & 5 \text{ years} \\
3.15 \times 10^7 & 1 \text{ year} \\
2.68 \times 10^6 & 1 \text{ month} \\
8.64 \times 10^4 & 1 \text{ day} \\
3.60 \times 10^3 & 1 \text{ hour} \\
\hline
\end{array}
\]

On closer analysis of Figure 5.18, it can be interpreted that the data points for the dynamic flexural modulus shift factors are better fitted by two lines, as shown in Figure 5.19. This suggests a non-uniform temperature dependent activation energy and thus reduces confidence in the validity of the time-temperature superposition principle, when applied to highly oriented PP. However, since these trend lines are still of a similar gradient, it is likely that the effect is negligible over this
relatively small range of temperature. This further illustrates the complexity of modelling the PP as a thermo-rheologically simple polymer.

![Graph showing non-uniform activation energy for time temperature superposition of dynamic modulus](image)

**Figure 5.19.** Non-uniform activation energy for time temperature superposition of dynamic modulus

### 5.4 Conclusion

Viscoelastic materials such as semi-crystalline polymers possess mechanical properties that are highly dependant on the temperature and strain rate at which they are applied. By orienting the amorphous phase in semi-crystalline polypropylene it is possible to reduce the dramatic decrease in stiffness normally seen at \( T_g \). By doing so the stability of the mechanical properties can be greatly improved in the region between -40°C and 120°C.

Despite the wholly thermoplastic nature of All-PP composites, the strength and modulus compare well to GMT. The tensile strength exceeded that of GMT at all temperatures investigated, while the tensile modulus possessed a higher modulus at low temperatures, but a slightly lower modulus at high temperatures. The heat deflection temperature was simulated using a dynamic test method and showed that the HDT of the All-PP composites tested was 20°C less than that of GMT or woven glass reinforced PP, but was far superior to that of isotropic PP.

Mastercurves were successfully produced using an Arrhenius equation to shift data in the time scale. Although, they may not be highly accurate for extreme strain rates, these mastercurves can be used to predict the behaviour of the material outside the time scales tested, but do not account for degradation due to environmental conditions.
Chapter 6

Impact Performance of All-PP Composites

6.1 Introduction

All engineering structures will experience impact within their service lives. The response of the material to impact loading will depend on various factors such as the geometry of the structure and striker, the mass and velocity of the striker, and frequency of impacts. Due to their high strength and stiffness, and good energy absorption due to delaminating failure modes, composite materials generally perform well in impact applications. Carbon and glass fibres suffer from a lack of plasticity which means that non penetrative impact loads can lead to (often invisible, subsurface) fibre damage, which can drastically reduce the residual mechanical properties of the composite. Thermoplastic fibre composites typically possess sufficient elastic limits to make them less sensitive to damage from lower energy impacts.

Thermoplastic fibres such as UHMW-PE have specific applications as impact defence materials, such as personal protection for military/police personnel from direct projectile impact (Jacobs and van Dingenen, 2001), or as spall liners behind ceramic/metallic armour in armoured vehicles to limit proliferation of shrapnel inside a vehicle following impact (Beugels, 2001). Composite ballistic protection can also provide significant weight savings for automotive defence, compared to steel armour (Tarim et al., 2001; Findik and Tarim, 2003) and has been assessed as fragment barriers for commercial aircraft (Shockey et al., 1999). The impact performance of composites has been modelled with some success to determine the methods of predict deformation (Dean and Wright, 2003) and model energy absorption (Morye et al., 2000).

In order to analyse the behaviour of materials under impact loading, there are numerous laboratory tests which can be performed, including notched or un-notched pendulum impact (Charpy and Izod), falling weight impact, projectiles fired by pneumatic guns, and lab-scale ballistic assemblies. The falling weight impact assemblies often use a force transducer to measure force upon impact, whereas ballistic impact methods employ a statistical approach to determine impact performance. Falling weight impact testing can provide analytical information about the mechanism on impact such as specimen displacement, duration of impact and energy absorption, but are limited to lower
velocities, <10m.s⁻¹. The main difference between falling weight impact and ballistic impact is the velocity of testing, and this can result in a different response by the material. In composite systems, ballistic impacts (typically >250m.s⁻¹) involve the propagation of transverse and longitudinal waves through the specimen, which are not seen in lower velocity impacts (typically <15m.s⁻¹). These transverse waves propagate through the thickness of the specimen, while the longitudinal waves propagate along the fibres at the sonic velocity of the reinforcement, $V_s$

$$V_s = \sqrt{\frac{E}{\rho}}$$  \hspace{1cm} 6.1

A large sonic velocity will allow the dispersion of energy to as large an area as possible, before local strain at impact site leads to failure. The specific energy absorption capability, $e_{sp}$, has also been proposed as a comparative tool for ballistic fibres (Jacobs and van Dingenen, 2001):

$$e_{sp} = \frac{\sigma \varepsilon}{2\rho}$$  \hspace{1cm} 6.2

Where $e_{sp}$ = Specific energy absorption capability
$\sigma$ = Tensile strength of fibre
$\varepsilon$ = Failure strain of fibre (%)
$\rho$ = Tape density

Figure 6.1 compares sonic velocity and specific energy absorption capability for some common reinforcing fibres. Equally performing composites shall be considered to absorb the same energy upon impact. The energy absorption can be described to affect a circular area of composite of radius, $r$, with an energy absorption described by the specific energy absorption capability, $e_{sp}$.

Since the radius of material absorbing impact is due to the transmission of a longitudinal stress wave in the fibres at $V_s$, the area, $a$, of material absorbing impact energy could be described by:

$$a = \pi r^2$$  \hspace{1cm} 6.3

or,

$$a \propto \pi V_s^2$$  \hspace{1cm} 6.4

Equally performing composites would absorb equal energy, so energy absorbed in this area could be designated, $c^2$:

$$c^2 = \pi V_s^2 \times e_{sp}$$  \hspace{1cm} 6.5

Combining constants, gives:

$$c = V_s \times \sqrt{e_{sp}}$$  \hspace{1cm} 6.6
Figure 6.1. Specific energy absorption capability index vs. sonic velocity for various fibres
(UWMW-PP data from Kristiansen et al., 2003)

Since graphically in Figure 6.1, axes are $V_s$ and $e_{sp}$, equation 6.6 represents a curve which describes two materials which have equal performance based solely on these two parameters. However, this curve only accounts for the two criteria of sonic velocity and specific energy absorption capability of the fibres as described in Figure 6.1. It can be seen that neither the highest draw ratio PP tapes described in Chapter 2, nor a highly oriented UHMW-PP fibre (Kristiansen et al., 2003) feature highly in either axis and so would be unlikely candidates for ballistic applications. In fact, both the PP tape and the UWMW-PP fibre show equal performance on this graph, since both points fall on the curve of equivalent performance for PP tapes. Using the design criteria described above, it can be seen that the PP tape used in this research would have a performance just below that of aramid fibres. Thus high modulus, high strength, low density and large strain to failure are required to provide good ballistic impact resistance, but this method does not exhaustively determine the suitability of a reinforcing fibre for a ballistic application, due to the range in possible energy absorption methods during ballistic impact, and also the fibre architecture within the composite.

One of the main performance indicators for ballistic performance is the V50 number. This merely gives the velocity at which a particular specimen will stop 50% of a certain type of projectile fired at it (Taylor and Carr, 1999). Thus a material can have a range V50 values, each referring to a specific projectile or specimen thickness. Another value which is perhaps more useful to compare different materials is the energy per areal density absorbed by a material, which considers specimen dimensions, density and energy of the projectile. This research considers impact from falling weighted striker and also ballistic impact by 9mm full metal jacket (FMJ) parabellum projectiles and 1.1g (17grain) fragment simulating projectiles (FSPs). FSPs are machined steel cylinders which...
simulate projectiles from fragmentation grenades or shrapnel from explosions (Iremonger and Went, 1996). Figure 6.2 shows a 1.1g FSP, on the left hand side, next to a plastic firing sabot on the right. 9mm bullets are considered here because they are typical projectiles from common handguns.

There are a range of different international ballistic standards which specify the energy per areal density of a material that is required to stop a given type of projectile. One of the most popular of these is the American National Institute of Justice (NIJ) range of standards which specify that a minimum number of ballistic projectiles must be stopped by a defined area of specimen.

Despite Figure 6.1 indicating that PP is unlikely to be an ideal candidate for highly impact resistant applications, the very high volume fraction of fibre present in All-PP composites compared to traditional composites, combined with their low density may enhance their competitiveness. To determine the energy absorbed during impact, falling weight impact tests are performed on woven fabric All-PP plates manufactured with varying compaction pressure and temperatures. The effect of these parameters on the tensile and compressive properties of All-PP composites has already been established (see Chapter 4). By altering the composite processing conditions, the interfacial properties and density of All-PP plates can also be controlled, and this effect on impact resistance will be determined. In addition to the effect of processing conditions, the effect of impact velocity and testing temperature will also be determined, since it is important to establish the behaviour of All-PP composite in a range of possible conditions. Finally, the ballistic impact resistance of All-PP plates will be determined, and compared to current ballistic commercial materials.
6.2 Experimental Procedure

6.2.1 Penetrative Falling Weight Impact Testing

Penetrative falling weight impact tests were performed as described by ASTM 5628-96 (using ‘FE’ geometry), on a range of woven All-PP composite plates. The specimens were created from plates of woven All-PP fabric as described in previous chapters for mechanical testing. This test machine used is manufactured by Ceast, Italy, and has a 10mm radius hemispherical striker suspended at a measured height, which upon release falls freely to strike the specimen fixed in a circular aperture beneath. A cut away schematic of the impact aperture is shown in Figure 6.3, in which the test specimen is also shown.

The impact striker contains a force transducer which measures the force upon impact, and this force/time provides a measurement of the energy absorbed by the impact (Kalthoff, 1993). The force/time curve is first integrated, to give the area under the curve, \( A_{\text{total}} \) (ISO, 1989):

\[
A_{\text{total}} = \int_{0}^{\infty} F(t)dt
\]

6.7
Subsequently, the energy absorbed by impact, $E_{\text{impact}}$, can be calculated by:

$$E_{\text{total}} = v_0 \times A_{\text{total}} \left(1 - \frac{v_0 A_{\text{total}}}{4E_S}\right)$$

Where

- $E_{\text{total}}$ = Total energy of impact
- $v_0$ = Impact velocity
- $A_{\text{total}}$ = Area under force/time curve
- $E_S$ = Energy of striker

It is possible to alter the energy of the striker by varying the initial height or the mass on the striker. In these tests, height is kept constant at 1m and mass varied in order to vary impact energy while maintaining constant impact velocity. For penetrative impact tests, the initial energy is always at least twice the energy absorbed in penetration in order to achieve an accurate measurement. Energy losses due to friction in falling, sound, and heat are negligible, so will be ignored.

### 6.2.2 Non-Penetrative Falling Weight Impact Testing

Non-penetrating impact tests were performed to investigate the mechanisms of impact damage on All-PP plates. Tests were performed on a similar Ceast falling weight impact machine with an identical striker, but also equipped with a mechanism to catch the striker on rebound from initial impact, and prevent further strikes. Again, the impact energy is controlled by adding or removing mass from the striker. Prior to testing, specimens were airbrushed with a fine, random, high contrast speckle pattern. High resolution images of these surfaces were captured using an ARAMIS 3D strain mapping system manufactured by GOM GmbH (Germany), equipped with two Vosskühler CCD 1300F high resolution digital cameras (Tyson et al., 2002). Following impact, images of the specimens were captured again, and the ARAMIS software can produce a three dimensional map of the surface deformation due to impact damage. This requires the speckle pattern to remain intact during impact, and so complete maps cannot be produced if the surface layer is damaged or the pattern is removed by abrasion with the impact striker or gripping mechanism. The application of digital surface strain mapping has been successfully applied to bi-directional thermoplastic composites undergoing similar deformation due to stamping rather than non-penetrative impact (Martin et al., 1997) and has been applied to the thermoforming of All-PP composites elsewhere (Cabrera, 2004).

A more traditional method for assessing damage in non-penetrating impact of composites is ultrasonic C-scan, but as this method relies on varying densities within a fluid medium, typically water, it cannot easily be applied for a material such as polypropylene with a density so close to the density of water, 1g.cm$^{-3}$. The acoustic damping and the lack of large scale delaminations of tough materials such as polypropylene also reduce the efficiency of ultrasound scanning methods.
6.2.3 Strain Rate and Temperature Dependent Impact Resistance

In Chapter 5, it was shown that the mechanical behaviour of oriented PP tapes and woven tape All-PP composites depends on the strain rate and temperature. Penetrative impact tests were performed at a range of discrete temperatures in the range -40°C to 120°C, to determine the effect of temperature on the impact strength of woven tape composite plates. Plates were produced at a compaction pressure of 4MPa and a temperature of 140°C. Impact tests were performed using a Zwick Rel tensile testing machine fitted with an environmental chamber and an impact striker containing a force transducer similar to that described in this chapter, but with a striker radius of 5mm and a specimen holder aperture of 20mm. Hence energy values obtained here are not directly comparable to other impact tests within this thesis, since the striker geometry is smaller. The tests were performed at impact speeds of 10, 4, 1 and 0.1m.s⁻¹, to determine the effect of impact speed on the impact strength. The chamber temperature was heated by a circulating air oven and cooled by liquid nitrogen. As before, the specimens were placed in the chamber at room temperature and then the chamber was heated/cooled to achieve desired testing temperature. The specimen was allowed to stabilise for 10 minutes at the test temperature before testing. The temperature of the specimen was monitored externally using a thermocouple mounted in the specimen holder; this is important since unlike tensile tests there is a large contact area between impact specimen and holder. The impact striker, mounted on the crosshead, is pushed through the specimen at constant speed and the force recorded. The penetration energy is defined as the total energy absorbed by impact, which is the integral of the force time curve during penetration.

6.2.4 Ballistic Impact Testing

The impact velocity of falling weight impact tests from a height of 1m is 4.4m.s⁻¹, whereas ballistic impacts possess a typical impact velocity two orders of magnitude greater. In order to establish the ballistic performance of All-PP composites, plates of woven fabric plies were manufactured as described in Chapter 4 by a vacuum bagging route, and compacted with a pressure of 0.1MPa and 125°C. These processing conditions were selected as they provided the optimum impact performance, as will be shown subsequently in this chapter. These plates were subjected to ballistic impact by 8g, 9mm parabellum projectiles and 1.1g FSPs, using a ballistic firing set-up at DSM High Performance Fibres, Heerlen, The Netherlands. A schematic of the ballistic test set-up is shown in Figure 6.4, in which the total distance from firing barrel to mounted specimen is approximately 10m. The projectile is mounted in front of a charge inside the firing chamber. The 1.1g FSP is fired in a plastic sabot which falls away from the projectile upon exit from the barrel. The velocity of the projectile is approximately controlled by altering the volume of air in the chamber behind the projectile. A greater volume of air behind the projectile will lead to a lower pressure increase on combustion, and so a lower velocity of the projectile from the barrel. Thus by incrementally altering this air volume, exit velocity of the projectile can be approximately controlled. On firing, the projectile passes through two infrared gates that measure the velocity of the particle from the difference in time between passing each of the gates. As these gates are very close to the specimen (<1m), it is assumed that this is the impact velocity.
The specimen is mounted on a thick (15cm) plasticine backing which catches projectiles which penetrate the test specimen, and also allows for some out-of-plane displacement of the specimen. An impacted specimen is shown in Figure 6.5, in which the back surface of specimen is visible on the right hand side of the image, next to the plasticine backing material. In the case shown in Figure 6.5, all impacts have penetrated and there is a series of large deformations in the plasticine. Although, unlike a bullet, a FSP can tumble during flight, no account is made for the orientation of the FSP as it strikes the specimen.
6.3 Results and Discussion

6.3.1 Penetrative Impact Performance

Due to the dimensional effect of processing conditions on the compaction of All-PP specimens, as discussed in Chapter 4, it is important to determine the geometrical effect due to different specimen dimensions on the impact performance. Figure 6.6 shows the effect of specimen thickness on penetrative impact resistance for two different All-PP fabrics, with a woven glass–PP for comparison. All-PP fabrics 17-10(170) and 8-20(160) are summarised in Table 6.1.

Table 6.1. Details of All-PP fabrics 17-10(170) and 8-20(160)

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Tape Draw Ratio</th>
<th>Relative Tape Composition [A:B:A]</th>
<th>Drawing Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-10(170)</td>
<td>17</td>
<td>5:90:5</td>
<td>170</td>
</tr>
<tr>
<td>8-20(160)</td>
<td>8</td>
<td>10:80:10</td>
<td>160</td>
</tr>
</tbody>
</table>

As described in Chapter 3, fabric 8-20(160) is woven from a tape with a lower draw ratio, and so greater ply thickness. This leads to a greater thickness for the same number of plies compared to fabric 17-10(170). Figure 6.6 also shows a comparison of thickness with number of plies (shown in brackets). For specimens less than 2mm thick, there is clearly a non-linear relationship between specimen thickness and penetrative energy for All-PP composites.

Figure 6.6. Impact energy vs. specimen thickness
This is explained by examining the force-time curves of the impact penetrations for different thickness of All-PP composites. Figure 6.7 shows four typical force-time curves for fabric 17-10(170). For thicker specimens, behaviour is very similar, with maximum force increasing with specimen thickness. For specimens with a thickness of 1.2mm, a greater time to reach maximum force is observed. This is due to increased deflection of the specimen upon impact; very thin specimens exhibit greater flexural deformation. This will lead to a greater impact duration and a greater energy absorption, and so very thin specimens show a disproportional penetrative energy compared to their relative thickness (see Figure 6.8).

Figure 6.7. Force vs. time curves of typical All-PP composites with varying thickness

Figure 6.8. Impact energy normalised for specimen thickness vs. specimen thickness
Considering this non-linearity, all further impact tests are performed on specimens above 2mm, so that thickness can be normalized in the approximately linear region of the impact energy/thickness relationship. In any case, the impact performance of the All-PP composites described in this chapter can be considered a minimum performance, since this thickness of All-PP composites gives the lowest impact performance.

Previous chapters have shown that the mechanical properties of All-PP composites are determined by processing parameters and this is also true of impact energy absorption. Figure 6.9 shows the effect of compaction temperature on the impact resistance of All-PP plates, compared to PP strengthened with ‘foreign’ reinforcements: woven glass reinforced polypropylene (Twintex®, 40% wt), glass-mat reinforced polypropylene (GMT, Symalite®, 23% wt) and flax fibre reinforced polypropylene (NMT, 40% wt).

![Figure 6.9. Impact energy vs. compaction temperature](image)

These traditional composites are represented as horizontal lines even though impregnation/consolidation are not necessarily viable across this temperature window. For both All-PP fabrics, there is a general decrease in absorbed impact energy with increasing compaction temperature.

As the tensile strength of woven All-PP composite plates processed at the same compaction pressure is largely independent of compaction temperature within the range of temperatures shown here, (see Figure 4.18) the change in absorbed impact energy with compaction temperature can be traced to changes in the interfacial strength. Figure 6.10 combines the absorbed impact energy of fabrics 17-10(170) and 8-20(160) with adhesive strength determined from T-Peel tests of single tapes of 17-10(170) and 8-20(160). These properties are clearly linked, with impact strength being inversely related to the interfacial strength of the tapes.
At low compaction temperatures, the interface is relatively weak and so debonding is the preferential mechanism of impact failure. This delamination, fibrillation and tape pull-out are highly energy consuming processes. As compaction temperature is increased, the interface becomes stronger and so the dominant mechanism of failure appears to be tape failure very locally to the impact site. Thus at lower compaction temperatures, as the interface is weaker, the energy absorbed is less localised and the absorbed impact energy is greater (Morye et al., 2000; Harel et al., 2002); the same effect has been reported for hot compacted gel-spun UHMW-PE fibres composites (Morye et al., 1999). As in interfacial studies of Chapter 3, because the temperature processing window of fabric 17-10(170) is much wider than that of fabric 8-20(160), the effect of temperature on absorbed impact energy is much less dramatic in fabric 17-10(170) than fabric 8-20(160). This also makes fabric 17-10(170) a more easily processable and consistent material.

As with the tensile properties, the pressure at which the All-PP composites are compacted also affects impact properties. Figure 6.11 shows the effect of compaction pressure on the impact performance of fabric 17-10(170), again with woven glass PP, GMT and NMT for comparison. The All-PP specimens have been compacted at three different pressures of 0.1MPa (compacted via vacuum bagging), 1.8MPa and 11.4MPa (compacted via hot pressing) as described in Chapter 4. Here it is clear that All-PP composites can easily compete on impact performance with the woven glass PP tested. As compaction pressure of the All-PP composites increases, absorbed impact energy is reduced. This is due to an increase in interfacial strength with increasing compaction pressure, as seen before for increasing compaction temperature. At all compaction pressures, an approximately constant absorbed impact energy is seen over the range of temperatures tested.
Due to the relatively low density of bulk PP and even lower density of All-PP composites (see Figure 4.23), these composite plates perform very well when specific impact energy is considered. Figure 6.12 shows the specific performances of these All-PP plates compared to woven glass PP, GMT and NMT, all normalised for density. From these results, all of the All-PP plates out-perform each of the alternatives considered here (see Table 6.2).
Table 6.2. Summary of penetrative impact performance by falling mass test
(* Impact properties of All-PP composites depend on processing conditions)

<table>
<thead>
<tr>
<th>Material</th>
<th>Fibre Weight Fraction [%]</th>
<th>Density [g.cm(^{-3})]</th>
<th>Penetrative Energy [J.mm(^{-1})]</th>
<th>Specific Penetrative Energy [kJ.g(^{-1}).mm(^{2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>All-PP</td>
<td>-</td>
<td>0.61 - 0.91</td>
<td>21.4 - 44.9*</td>
<td>25.4 - 73.7*</td>
</tr>
<tr>
<td>Woven Glass/PP</td>
<td>40</td>
<td>1.24</td>
<td>28.4</td>
<td>22.9</td>
</tr>
<tr>
<td>GMT</td>
<td>23</td>
<td>1.07</td>
<td>9.8</td>
<td>9.2</td>
</tr>
<tr>
<td>NMT</td>
<td>40</td>
<td>1.15</td>
<td>4.5</td>
<td>3.9</td>
</tr>
</tbody>
</table>

This transition in failure mode can be most clearly seen in post impact specimens which have been compacted at different temperatures and pressures (see Figure 6.13). By comparing an All-PP plate which has been compacted at a low temperature and low pressure (140°C, 0.1MPa), with an All-PP plate which has been compacted at a high temperature and high pressure (160°C, 11.4MPa), the energy absorption mechanisms of plates which exhibit the highest and lowest impact energy absorption, respectively, can be investigated. Figure 6.13a shows an impacted specimen which has been compacted at low temperature and pressure (140°C, 0.1MPa) and shows large amounts of fibrillation and delamination, and a higher energy absorption. Figure 6.13b shows a similar specimen which has been processed at high temperature and pressure (160°C, 11.4MPa) and shows a characteristic ‘star’-shaped penetration which is formed by tape breakage and tearing along tape boundaries. This is a lower, more localised energy absorption, since the deformation is limited to the immediate impact site, unlike the specimen compacted at 140°C, 0.1MPa which shows larger deformations in the plane of the specimen, in the area surrounding the impact site.

Figure 6.13. Typical impact penetration damage at different compaction temperatures and pressures
(a) 140°C, 0.1MPa and (b) 160°C, 11.4MPa
Ignoring frictional losses, the energy absorbed upon falling weight impact, $E_{\text{total}}$, can be considered as follows:

$$E_{\text{total}} = E_T + E_I$$

6.9

Where $E_T = \text{Energy absorbed by plastic tape deformation}$

$E_I = \text{Energy absorbed by interfacial failure}$

The energy absorbed by tape deformation, $E_T$, will be dictated by the tensile behaviour of the composite. Since penetration requires tape failure, the energy absorption during impact can be compared to energy absorption during tensile testing of virgin tape and consolidated All-PP composites. If the impact load is considered to be solely absorbed by tapes that pass through the impact site, an effective volume of tape which is loaded upon impact can be calculated (Peijs et al., 1994).

The effective tape volume can be modelled by considering the All-PP plate as stacked, unconsolidated tapes by ignoring interfacial properties and crimping, and solely considering tensile properties of the tape. Alternatively, to account for the effect of tape interactions, crimping, and the effects of composite processing, the tensile properties of woven specimens tested in the $0^\circ/90^\circ$ direction can be considered (see Chapter 4). In either case, the volume loaded in tension can be considered as two rectangular sections running normal to one another with the impact site at the centre (see Figure 6.14). Although the strain rate applied in impact ($10^{-2} \sim 10^{-3}\text{s}^{-1}$) is greater than that applied in the tensile tests ($2.5 \times 10^{-4}$), Figure 5.17 showed that tensile strength and modulus are relatively consistent ($\pm 15\%$) over the strain rates seen here, and so absorbed energy is assumed to be similar.

![Figure 6.14. Schematic of effective area of tapes loaded in tension during impact](image)
Since impact energies are normalised for specimen thickness, specimen thickness can be ignored, and rather than considering effective tape volume, the effective tape area, $A_{ET}$, can be given by equation 6.10.

$$A_{ET} = 2abV_fV'_f$$

Where $a = \text{Striker diameter, 20mm}$

$b = \text{Effective tape length, 60mm}$

$V_f = \text{Volume fraction of tape in composite, } \approx 1$

$V'_f = \text{Volume fraction of effective material in loading direction}$

To model impact based on stacked, unconsolidated tapes, $V'_f = 0.5$ since half of the tapes will be running normal to the direction of loading, and so make no contribution to tensile energy absorption. To model impact based on compacted woven plies, $V'_f = 1$, since the tensile behaviour of the woven tape composite already accounts for ineffective tapes in the fabric oriented at 90° to the loading direction. Table 6.3 shows the energy absorbed by tensile failure of the tape together with woven tape composite tensile specimens (see Chapter 4) obtained by integrating the area under stress vs. strains curves obtained during tensile testing. Combining this data with the energy absorbed by penetrative impact (see Figure 6.11), shows that the energy absorbed solely by tensile failure of tapes is very close to the energy absorbed by impact failure of a woven tape composite specimen compacted 160°C and 11.4MPa, of which 96% can be attributed to tape failure.

Table 6.3. Energy absorption mechanism of All-PP composites

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tape</th>
<th>Compacted Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compaction Temperature [°C]</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>Compaction Pressure [MPa]</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Energy Absorbed by Impact Failure (per unit thickness)</td>
<td>$4.5 \times 10^4$</td>
<td>$2.5 \times 10^4$</td>
</tr>
<tr>
<td>Energy Absorbed by Tensile Failure [J.m$^{-3}$]</td>
<td>$2.24 \times 10^7$</td>
<td>$5.2 \times 10^6$</td>
</tr>
<tr>
<td>Effective Impact Area Loaded in Tension [m$^2$]</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$2.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Energy Absorbed by Tape in Effective Impact Area (per unit thickness) [J.m$^{-1}$]</td>
<td>$2.69 \times 10^4$</td>
<td>$1.2 \times 10^4$</td>
</tr>
<tr>
<td>Percentage of Impact Energy Absorbed by Tape Failure</td>
<td>27%</td>
<td>96%</td>
</tr>
</tbody>
</table>
However, the composite plate specimen compacted at 140°C and 0.1MPa shows much greater energy absorption than can be solely attributed to tensile failure of the tapes, which in this case is only 27%. Since composite plates processed under this combination of low pressure and temperature possess much lower interfacial strengths, it is clear that here a large amount of energy is absorbed by fibre pullout or debonding. It is likely that the combination of a weak interface with stiff, strong tapes has a synergistic effect on the energy absorption of All-PP composites during impact, by allowing distribution of impact loading to a greater volume of tape. The fibre pullout is clearly visible from the difference in out of plane deformation of the two samples, as shown in Figure 6.15.

![Figure 6.15](image)

*Figure 6.15. Illustration of the out of plane deformation of All-PP composites compacted at (a) 140°C, 0.1MPa and (b) 160°C, 11.4MPa*

It is worth noting, that although one can optimise absorbed impact energy through the control of the interface, this may result in a composite that has such poor interfacial strength that it may be unsuitable for some structural applications. This shows that composites properties can be tailored through the interface in the final processing step to suit the composite application. This is a unique feature of All-PP composites compared to traditional composites which have an interface controlled fibre matrix interaction which cannot be altered after production.

### 6.3.2 Analysis of Non-Penetrative Falling Weight Impact Damage

In order to assess the damage tolerance of All-PP composites, non-penetrating impact tests were performed on a range of specimens manufactured from fabric 17-10(170) with three different compaction temperatures, but constant pressure (4MPa). These specimens were impacted with a constant energy of 20J and the tensile surfaces were analysed with an ARAMIS digital optical strain mapping system. The major surface strains on the tensile side due to the impact were compared and are presented in Figures 6.16a-c. A more detailed optical analysis of non-penetrative impact deformation can be found in the original thesis discussing this research (Alcock, 2004). The strain maps show discontinuities of strain (shown as holes in the diagrams) which are due to surface damage. Clearly visible on all images is also the circular pattern of the specimen clamp; this is shown as either a ring of high strain due to surface deformation, or by discontinuous strain mapping due to removal of the surface pattern by the clamp. In the strain mapping sections detailed below,
specimens are oriented with tapes running approximately horizontally and vertically in the plane of the page.

**Figure 6.16a.** Tensile surface of All-PP plate compacted at 125 °C and impacted with 20J

**Figure 6.16b.** Tensile surface of All-PP plate compacted at 140 °C and impacted with 20J

**Figure 6.16c.** Tensile surface of All-PP plate compacted at 160 °C and impacted with 20J
### Table 6.4. Summary of non-penetrative impact specimen figures

<table>
<thead>
<tr>
<th>Compaction Temperature [°C]</th>
<th>Impact Energy [J]</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>10</td>
<td>6.16a</td>
</tr>
<tr>
<td>140</td>
<td>20</td>
<td>6.16b</td>
</tr>
<tr>
<td>140</td>
<td>30</td>
<td>6.16c</td>
</tr>
</tbody>
</table>

Figures 6.16a, 6.16b and 6.16c show a range of damage processes for the specimens compacted at 125°C, 140°C and 160°C respectively, and subjected to a 20J impact. As compaction temperature increases from 125°C to 160°C (from Figure 6.16a – 6.16c) there is a transition from anisotropic behaviour to a more isotropic state, and the areas of greatest strain are located in regions at ±45° to the tape directions. This is because the tensile modulus of composites loaded in the ±45° direction is approximately 40% to that of the 0° (tape) direction (see Figure 4.9), so stress in this direction is much more easily relieved by deformation through interply shearing. This is illustrated in Figure 6.17. Figure 6.18 shows the stress/strain curves of two woven plates compacted at 140°C and 160°C, and tested at 0°/90° and ±45° to the tape direction. This illustrates the difference in moduli, but also the difference in elastic limits of 0°/90° and ±45° specimens. It is likely that there is some strain in the 0° and 90° direction tapes in the impacted plate, but this is elastic strain which is dissipated in the rebound of the striker, and not visible in the post impact specimens, whereas the strain in the ±45° direction to the tapes is plastic and so is seen in the post impact strain map.

![Figure 6.17. Stress dispersion in different angles to tape direction](image)

This directional change in modulus is also affected by compaction temperature; specimens compacted at 125°C possess poor interfacial bonding and thus surface tapes will be much freer to shear (the ‘trellis’ effect), than those compacted at 160°C which will be much more firmly locked in position. Thus increased compaction temperatures lead to a more homogenous system.
Figure 6.18. Typical stress vs. strain curves for woven tape composite specimens loaded in tension at $0^\circ/90^\circ$ and $\pm 45^\circ$ to the tape direction

Figure 6.19. Illustrating orientation of strain sections for Figures 6.19 and 6.20

Figure 6.20 illustrates the effect of the consolidation on the strain of the surface tapes. The graph represents the major strain as a function of the radial distance from the centre of the impact site (20mm is the radius of the clamped region) for two sections at $0^\circ$ and $\pm 45^\circ$ to the tape direction (see Figure 6.19). The specimen compacted at 125°C shows that strain in the section radiating in the $0^\circ$ direction decreases with increasing distance for impact site, as would be expected, but more importantly, much greater strains are seen in the section radiating at $\pm 45^\circ$ to the tape direction. This shows the heterogeneity of strain distribution in this specimen. Contrary to this, the specimen compacted at 160°C shows very similar strain distribution whether a section is taken at $0^\circ$ or $\pm 45^\circ$ to the tape direction.
It can also be seen that the plastic deformation due to the striker at the impact site is much greater for the specimen compacted at 125°C than at 160°C. This implies that the specimen compacted at 125°C, would have lower resistance to denting than the specimen compacted at 160°C, despite a greater penetration resistance. This is an important consideration for applications in which the material has to be resistant to surface damage as well as providing penetrative protection. The oscillations seen in the strain magnitude for the specimen shown in Figures 6.21, has a wavelength of approximately 4mm, and this can be explain by the fact that the strain is calculated on the surface of a woven fabric, with each tape being approximately 2mm wide. The peaks in the strain represent the tapes in the 0° direction which are running radially from the impact site in the 0° direction. The tapes which are perpendicular to these are not directly loaded and so show much lower strain. The specimen compacted at 160°C shows much less oscillation due to the increased bonding and superior load transfer as described above.

The use of optical strain mapping only provides information about surface strains, and since compressive and tensile faces show different strain situations, it is likely that while the surface strains indicate the through-thickness strain distribution, they cannot totally describe the strain distribution in a specimen. Since the outer surfaces of the specimen are gripped during impact, it is likely that greater strain is present in subsurface plies due to interply shearing following delamination. Thus information obtained by optical strain mapping must be considered as an indicative rather than an exhaustive description of the strain distribution, and thus energy absorption of a specimen.

**Figure 6.20.** Surface strain section of typical tensile face of impact specimen
6.3.3 Impact Performance of Composites at Elevated Temperatures

The penetration impact energy absorbed by All-PP plates, normalised for specimen thickness for a range of temperatures and strain rates is shown in Figure 6.21. The effect of impact temperature is clearly quite small. Since the temperature range passes through the glass transition temperature of polypropylene (approximately -10°C), a large difference would be expected in impact performance, since below T_g, semi-crystalline polymers have a much lower strain to failure and hence a lower resistance to crack propagation. This is characterised by low penetrative impact energy. However, Figure 5.5 and Figure 5.9 have already revealed the absence of a significant glass transition temperature in individual tapes or composites, respectively. Therefore, there is a slight increase in penetrative impact energy for composites at -40°C, but not the large decrease that would normally be associated with the impact performance of a semi-crystalline polymer below T_g.

![Figure 6.21](image)

**Figure 6.21.** Penetrative impact energy vs. impact speed for a range of impact temperatures

Figure 6.22 shows that the effect of impact speed is much greater than impact temperature. Attempts were made to assemble a meaningful mastercurve from this impact data as was done for tensile behaviour in Chapter 5, but the effect of the processing conditions investigated did not provide a clear behaviour. In tensile deformation, the temperature is inversely equivalent to strain rate, and a decrease in temperature or an increase in strain rate would have a similar effect. Figure 6.21 shows that decreasing temperature leads to an increase in absorbed impact energy, as does an increase in impact speed, but the effect due to increasing the impact speed is much greater. An increase in strain rate of two decades leads to a 10% increase in tensile strength (see Figure 5.16), but this alone cannot explain the mechanism behind the large increase in penetrative impact energy absorbed at impact speeds of 10m.s^{-1}. During penetrative impact of All-PP composites, numerous failure modes operate. On initial impact the composite is deformed in bending, this causes a tensile deformation in the constituent tapes, and tape debonding. These tapes ultimately fail in tension. The stiffness and strength of the tapes have been considered but not the
delamination process and delamination at higher speed is likely to be the cause of increased impact energy at higher strain rates.

![Figure 6.22. Penetrative impact energy vs. impact temperatures for a range of impact speed](image)

6.3.4 Ballistic Impact Performance

Ballistic analysis of the All-PP plates was performed to determine the effect of high-speed impact on All-PP plates. Specimens with the optimum performance in falling weight impact, compacted at 0.1MPa and 125°C, were chosen for ballistic analysis. Firstly, a panel with an areal density of approximately 8kg.m⁻² (~12mm thick) was tested with a 1.1g FSP to establish a V⁵₀ for this plate. The FSP used is shown in Figure 6.2, and has a diameter of 5.39mm and a length of 6.35mm. The mechanics of penetration have been investigated for FSP penetration of a nylon/EVA composite system (Iremonger and Went, 1996) and showed that failure in this system was mostly due to fibre breakage and shear ‘cutting’. For All-PP systems, it was apparent from the post impact specimens the energy absorption mechanism depends on the processing conditions. For All-PP composites with high compaction temperature and pressure, impact energy is almost solely absorbed by tape failure. However, All-PP specimens with lower compaction temperatures and pressures (and so also a weaker interfacial strength) showed large energy absorption by delocalised delamination. On this basis, All-PP specimens created for ballistic testing were based on low compaction temperature and pressure (125°C and 0.1MPa). The result of the V⁵₀ test can be seen in Figure 6.23. The V⁵₀ for the FSP, calculated as an average velocity of the final four values (two penetrating, two non-penetrating) is 504m.s⁻¹ and the energy per areal density is approximately 17J.kg⁻¹.m².

A similar V⁵₀ test was performed with a 9mm (8g) FMJ bullet. Because of the greater kinetic energy of the 9mm FMJ, a thicker plate is required to prevent penetration, but energy/areal density is
also greater, at 44J kg\(^{-1}\)m\(^2\). This performance is specific to the processing conditions for the All-PP composite, as the impact performance is expected to vary for ballistics as it does for falling weight impact. All of the V50 values will be slight underestimates as they do not consider the cumulative damage effect of numerous impact in the same test panel, although damage appears to be very localised (see Figure 6.5).

Figure 6.23. Ballistic V50 determination of an All-PP composite plate

Thus the mechanisms of energy absorption which operate to give All-PP composites a large impact resistance, i.e. highly delocalised delamination and tape debonding, are not witnessed in the very localised failure in ballistic impact. Figure 6.24 compares the energy per areal density of All-PP with some alternative polyolefin ballistic composites. Dyneema\textsuperscript{®} UDHB25 (DSM, 2002) is a composite based on high modulus polyethylene fibres arranged in unidirectional plies between polyolefin films, which are then compacted into a composite by the application of heat and pressure. Dyneema\textsuperscript{®} UD66 is a similar product which has been tested independently (Morye et al., 2000) and shows the same trend in behaviour as the data supplied by DSM for UDHB25. These composites are rigid plates rather than loose fabrics and are often designed to prevent penetration by small bullets (such as 9mm FMJs). Dyneema\textsuperscript{®} Fraglight is a felt made up of the same Dyneema\textsuperscript{®} yarn but is an unconsolidated, flexible textile which is optimised to prevent penetration by FSPs.

In order to prevent penetration by low mass FSPs, such materials are designed as loose fabrics which can absorb energy by large deformations out of the plane of the material, rather than solely fibre breakage and delamination in the fabric plane (Taylor and Carr, 1999; Lee et al., 2001). This out-of-plane deformation mechanism is impossible in the All-PP plates used here because of the low density giving a high thickness, leading to an increased flexural strength, as can be seen in the tested specimen shown in Figure 6.5.
Also shown in Figure 6.24 is a polyethylene/polyethylene composite which has been investigated for possible ballistic applications (Harel et al., 2002). This material is composed of unidirectional Dyneema® fibres hot compacted between films of high density polyethylene. Such polyethylene/polyethylene composites have a fibre volume fraction of 72%, and similar to All-PP composites should be easily recyclable. Since the ideal ballistic material would absorb most energy while having the lowest areal density, the performance of All-PP is slightly better against the 9mm FMJs than the FSPs, but it is clear that all of the alternative polyolefin materials considered here easily out-perform this specific All-PP plate in these ballistic applications. It is also worth noting that all the other composite systems compared so far in this research are stacked UD layers rather than the woven plies which are used in All-PP. Stacked unidirectional plies possess greater energy absorbing potential because delaminations can more easily spread though the composite allowing a large damage area and so large energy absorption. This is partly due to the absence of crimping in stacked UD composites, and also partly due the increased interply plasticity of woven composites (Lee et al., 1994; Duarte et al., 1999; Kim and Sham, 2000; Jacobs and van Dingenen, 2001). This effect gives stacked UD composites a more suitable architecture for ballistic applications, before any consideration for actual material property is considered. A comparison of Dyneema® UDHB25 compared to a woven Dyneema® fabric composite showed a 25% increase in energy absorption of 2.85g FSPs, which is due simply to the composite architecture (Beugels, 2001). There may be a significant cost/performance factor which would make All-PP plates a viable cost-effective option for some types of ballistic impact, but just considering the results here they cannot compete with UHMW-PE alternatives solely on ballistic performance due to their inferior modulus and strength.
6.4 Conclusions

The impact performance of All-PP composite materials has been analysed through penetrating and non-penetrating impact by falling weight testing, and ballistic impact. From these results, some conclusions may be made; All-PP composite plates possess excellent resistance to falling weight impact penetration and can compete or outperform glass or natural fibre reinforced polypropylene. (See Table 6.2). As predicted by dynamic analysis, the normal glass transition temperature which results in a significant decrease in impact resistance of isotropic PP at low temperature (>0°C), is absent in All-PP composite due to the high molecular orientation. This means that unlike isotropic PP, All-PP composites retain their impact resistance at very low temperatures.

The dominant failure modes of All-PP composites in impact are delamination and tape fracture. Since the interfacial strength of All-PP composites is controlled by processing conditions, it is possible to tailor the impact resistance by altering compaction parameters. Impact performance increases with decreasing interfacial strength, with penetration energy increasing with decreasing compaction temperature and pressure. All-PP composites which are optimised for impact, however, may not possess adequate interfacial strengths to make them viable structural components. Alternatively, such All-PP composites may find applications as low-cost alternatives to current rigid ballistic protection materials which are aimed at protection from small fragments. A summary of the impact properties of All-PP composites plates is shown in Table 6.5.

Table 6.5. Summary of the effect of processing conditions on impact properties of All-PP composites

<table>
<thead>
<tr>
<th>Property</th>
<th>Increasing Compaction Temperature or Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>▲</td>
</tr>
<tr>
<td>Penetrative Impact Resistance</td>
<td>▼</td>
</tr>
<tr>
<td>Peel Strength</td>
<td>▲</td>
</tr>
<tr>
<td>Uniformity of Surface Strain</td>
<td>▲</td>
</tr>
</tbody>
</table>
Chapter 7

Processing of All-PP Composites

7.1 Introduction

So far the research presented in this thesis has concerned the performance of All-PP composites in controlled laboratory conditions. While this is a suitable method to characterise the mechanical properties of the material, some practical questions remain regarding the use of All-PP composites in real applications. It has been shown possible to create simple plates, but practical processing routes for various geometries will be discussed in this chapter. Also considered in this chapter will be an investigation to determine the recyclability of All-PP composites. Of course, considering the low price of virgin PP together with the low cost of disposal, recycling may not be economically viable, but the possibility of recycling All-PP tapes or composites to produce All-PP tapes with the same performance of the original All-PP tapes is desirable, especially in the light of current legislation on end of life vehicles.

Since the All-PP composites produced are entirely polypropylene, it is likely that the resistance of All-PP composites to degradation can be addressed by using the same anti-oxidant and UV blocking masterbatches that are applied to isotropic polypropylene. However, the effect of the structural changes due to drawing and composite consolidation, such as the thermal stability and porosity (see Chapter 4) must be addressed. The thermal stability of the composites can be predicted from the thermal stability of the tapes presented in Chapter 2, and the effect of temperature on the dynamic mechanical properties of All-PP tapes and composites has been discussed in Chapter 5. The effect of porosity on the performance of All-PP composites will now be addressed.

7.2 Fluid Absorption of All-PP Composites

By controlling the processing parameters during All-PP composite production, the density of the tapes and subsequent composites can be controlled. The density of the tapes is controlled by drawing conditions, which affect microvoiding within the tape, while the density of All-PP composites is controlled by composite consolidation conditions, which affects voiding between
adjacent tapes. The resulting low density of the final composite is perceived as beneficial from an application point of view since it implies that weight savings can be made by using All-PP composites to replace conventional composites. But there are also negative effects caused by these voids, particularly the risk of fluid absorption, which must be prevented particularly in applications such as automotive (Schuh, 1999). If the interply voids seen in Figure 4.24, are closed i.e. they are discrete, unconnected voids, the risk of fluid uptake is relatively low since fluid ingress would only occur near the surface of the composite. However, if these voids are continuous, the risk of fluid uptake is much greater. Although polypropylene is hydrophobic, capillary action will act to draw water between the fabric plies to fill the network of continuous voids. To assess the fluid uptake of All-PP panels, the weight gain of woven fabric All-PP plates following immersion in either hydraulic oil or distilled water has been measured.

To measure the weight gain due to water immersion, test specimens were made of 4 types of PP composites (2 types of All-PP composites compacted at 140°C and 0.1MPa and 4MPa respectively, GMT and NMT) and 1 isotropic PP as shown in Table 7.1, measuring 75mm x 25mm x 3.2mm in accordance with ASTM D570. The All-PP specimens were cut from plates processed by either vacuum bagging or hot pressing, as described in Chapter 4. These were dried in an oven for 24 hours at 60°C to remove initial moisture, and weighed to determine initial weight. These were then immersed in distilled water at 20°C for 1 month. Following immersion, the specimens were dried by hand with a dry cloth to remove surface water and weighed using a microbalance with an accuracy of ±1mg. Figure 7.1 shows that after 1 month (730 hours), the samples reach a maximum water uptake and are considered to be saturated.

To measure the absorption of oil by All-PP composites, a specimen compacted at 140°C and 4MPa, with the same dimensions as before, was immersed in a commercial hydraulic oil with a density of 0.87g.cm⁻³. Since it was not possible to completely remove surface oil by hand, the density of the All-PP plate was measured by the Archimedes principle as described in Chapter 2, but using oil as the fluid. Initially these All-PP specimens possess a density of 0.82g.cm⁻³, and float in the oil. The upthrust is measured by placing the specimen under an inverted basket to push upward, as was used to measure the density of All-PP tapes in water (see Chapter 2). However, as the oil is absorbed into the All-PP plate, the density of the specimen increases and exceeds that of the oil and so the specimen has to be moved above the basket to push downward.

<table>
<thead>
<tr>
<th>Material</th>
<th>Note</th>
<th>Density [g.cm⁻³]</th>
<th>Water Uptake [% weight]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic PP</td>
<td>C2 copolymer</td>
<td>0.91</td>
<td>0.03</td>
</tr>
<tr>
<td>GMT</td>
<td>23% wt fibre</td>
<td>1.07</td>
<td>0.6</td>
</tr>
<tr>
<td>NMT</td>
<td>40% wt fibre</td>
<td>1.15</td>
<td>5.5</td>
</tr>
<tr>
<td>All-PP</td>
<td>Compacted at 140°C, 4MPa</td>
<td>0.82</td>
<td>4.4</td>
</tr>
<tr>
<td>All-PP</td>
<td>Compacted at 140°C, 0.1MPa</td>
<td>0.68</td>
<td>22.3</td>
</tr>
</tbody>
</table>
It is clear from Table 7.1 that All-PP composites absorb water, certainly due to the interply voiding following compaction, since the isotropic PP specimen shows a negligible weight gain. This also proves that the interply voids are continuous within the composite. Figure 7.2 shows the weight percentage of oil absorbed as a function of time. Saturation is reached more rapidly with oil, after approximately 250 hours.

*Figure 7.1. Water absorption of an All-PP composite compared to GMT and NMT*

*Figure 7.2. Oil absorption of an All-PP plate*
The same All-PP plate absorbs a greater weight percentage of oil than water. This can be explained by considering the voiding present in the All-PP composites. The composites possess interply voids due to incomplete consolidation, but there are also microvoids present in the constituent tapes. If the All-PP plates are completely saturated by water, then the increased uptake of oil must be due to the absorption of oil by the tapes themselves. This hypothesis was proven by Cabrera, 2004, by the placing 0.1ml of oil on the surface of an uncompacted All-PP fabric. The fabric absorbed the oil and became transparent. Since a transition from transparent to opaque tape is seen by the creation of microvoiding during drawing (see Figure 2.14), the opacity is due to optical diffraction by these microvoids. Since the oil that is absorbed into these microvoids has a similar density to polypropylene, the optical diffraction is greatly reduced and the tape becomes transparent. A piece of fabric with oil applied to the surface is shown in Figure 7.3, and the transparency due to oil absorption can clearly be seen in the centre of the fabric revealing the Queen Mary logo underneath. This effect does not occur following the immersion of All-PP tapes in water.

![Image](image.jpg)

*Figure 7.3. Oil absorption by woven All-PP tapes (Courtesy of Cabrera, 2004)*

The water uptake of consolidated plates decreases with increasing compaction pressure; the All-PP composite compacted with 0.1MPa shows much greater water uptake than the All-PP composite compacted with 4MPa (see Table 7.1), as would be expected since the degree of porosity decreases with increasing compaction pressure as seen in Figure 4.24. However, both All-PP specimens tested show much greater water uptake than GMT. The uptake of oil occurs due to a combination of oil filling the interply voids as with water uptake but also by filling the microvoids within the tape structure.

### 7.3 Processing Routes of All-PP Composites

For All-PP products to be competitive, some consideration must be given to the range of possible routes to process these tapes or fabrics into finished products. The main focus on this thesis is the control of mechanical properties by tailoring the production of co-extruded PP tapes and
subsequently All-PP woven tape composite plates. These hot pressing and vacuum bagging routes are the most feasible to produce small scale planar test specimens but are discontinuous and so are unattractive for the large scale production of actual parts. A wide range of processing routes of All-PP composites is possible and these are considered in much greater detail by Cabrera, 2004.

In the production of any part, a significant contribution to the cost of the part is due to the processing route used. Of course, this contribution becomes greater when the material cost is small and a larger number of processing steps are involved. Since the material price of bulk PP is very low (currently 1-2€.kg\(^{-1}\)), the main contributor to the price of All-PP composites is in the process route chosen. The main processing routes applicable to manufacture All-PP composite parts are summarised in Figure 7.4.

Fundamental to the production of All-PP composites is the co-extrusion and drawing stage to produce a high quality tape with good mechanical properties. The use of co-extrusion and drawing is a continuous process, and several tapes (~20 tapes per co-extruder) can be produced simultaneously from a small industrial scale extruder at a typical rate of 100m.minute\(^{-1}\). This yields a production of approximately 60kg.hour\(^{-1}\) per tape (~1200kg.hour\(^{-1}\) per machine), using the commercial co-extrusion and drawing equipment described in Chapter 2 of this thesis. If the production of an All-PP filament wound part (see Figure 7.4) is desired, then the co-extrusion/drawing process together with the filament winding/consolidation process allow for comparatively rapid and cost effective part production. However, if an All-PP plate with bi-directional properties is required, a fabric weaving stage must be introduced. This stage is significantly slower than tape production and requires the use of several parallel weaving machines to weave the output of a single co-extrusion/drawing line.

The output of fabric of a single industrial weaving machine of the type used in current production is of the order of 60kg.hour\(^{-1}\), which is the output of a single tape. This can act as a bottleneck in production and requires significant investment for the acquisition of a large number of weaving machines. It is possible to go directly from woven fabrics to a finished tubular part via fabric pipe winding (see section 7.4), via vacuum forming or hot pressing All-PP sheets (see section 4.3.1) or directly thermoforming stacked fabrics.

Thermoforming plies of loose fabric is more complicated and slower than thermoforming preconsolidated sheets. For this reason, it is desirable to produce semi-finished sheets of All-PP composite, which can then be further formed. Since hot-pressing discrete sheets is a discontinuous, and thus slow process, an alternative method is suggested. All-PP sheets can be produced in a double belt press, as shown schematically in Figure 7.5. This is a continuous process in which plies of fabric are fed between two belts which apply pressure for the entire duration of the process. The maximum applicable pressure depends varies with machine design, but the maximum pressure applied by the double belt presses investigated in this research is of the order of 5MPa. These belts drag the fabric through heating and cooling zones which consolidate and cool the All-PP plate, respectively, so when the sheet leaves the double belt press it is sufficiently cooled to prevent shrinkage.
Figure 7.4. Main processing routes of All-PP composites
The use of a double belt press is much faster than producing All-PP plates in discrete stages in a hot press, since the use of hot press has a long cycle time due to heating and cooling of the mould during compaction. However, the use of a double belt press also requires a larger investment, and the output depends on the thickness of plates produced. If a number of thin plates of \( n \) plies thickness, are required it is possible to run large numbers of plies through separated by release films to prevent bonding between every \( n \)th ply of fabric. Therefore, output of double belt pressed plates can be increased.

A wide range of potential processing routes is facilitated by the large temperature processing window achieved by tape processing conditions. Three of these routes shall be described here with particular reference to peculiarities of applying these routes to All-PP composites: filament winding, thermoforming and sandwich panels.

### 7.3.1 Filament Winding All-PP Pipes

In a similar method to the production of unidirectional plate specimens detailed in Chapter 4, it is possible to create pipes or pressure vessels by filament winding tapes. Since a pressure vessel is essentially a pipe with closed ends produced by filament winding in three dimensions, pipe production routes are equally applicable to pressure vessel production. Unlike conventional thermoplastic composite filament winding processes, no heating is required during winding, but consolidation is achieved by winding and consolidating in two separate steps. Tape is cold wound onto a steel mandrel, and placed in a standard oven to heat and consolidate the composite. As seen previously for the production of T-peel specimens in Chapter 3, shrinkage of the tape during heating is opposed by the thermal expansion of the mandrel. Thus tape shrinkage and associated loss of tape properties is minimised. Following consolidation of the tapes, the steel pipe is removed from the oven and the thermal contraction of the steel mandrel on cooling allows easy removal of the All-PP pipe. The speed of this process is only limited by the maximum speed of the winding equipment, and the heating/cooling cycle of the oven, which, can simultaneously consolidate many pipes.

The structure of the pipe is determined by two important winding parameters: the displacement of the carriage per rotation of the mandrel, \( X \), and the angle of winding. If \( X \) is equal to the tape width, \( w \), each winding of tape will be placed next to the previous winding. If \( X > w \), the resulting pipe will be separated by a distance \( X-w \). If \( X < w \), the resulting pipe will
possess much greater tape crimping than a pipe wound with $X=w$. The winding angle determines the mechanical properties in the hoop direction of the pipe, analogous to the loading angle of unidirectional composites described in Chapter 4. The filament wound pipe considered here is composed of one inner hoop layer and three outer $\pm55^\circ$ layers. Some examples of these filament wound All-PP pipes are shown in Figure 7.6, which were produced using the filament winding facilities of the Swedish Institute of Composites (SICOMP, Sweden).

It is also possible to create pipes in a similar fashion by using strips of fabric instead of tape and consolidating in the same way. This method reduces winding time since with each winding rotation, a larger amount of material is wound, but for a winding angle of $0^\circ$, the proportion of tape acting in the hoop direction is 50%. Since the tapes oriented in the pipe axis direction are not constrained by winding, it is likely that relaxation will occur and mechanical properties may be lost in this direction.

To compare these methods of creating All-PP pipes, the hoop modulus of ring sections of four types of pipe consolidated at $140^\circ$C has been determined experimentally. The rings have an internal diameter of 145mm and a typical thickness of 1.5mm. The hoop modulus is determined by performing a split disc tensile test in accordance with ASTM D2291. In this test, a ring section of pipe is cut and placed over the split disc test assembly as shown in Figure 7.7. A crosshead displacement of 2.5mm.min$^{-1}$ is applied by an Instron tensile testing machine fitted with a 5kN load cell. The modulus is determined by using strain gauges fixed to the ring section of pipe and is determined at a strain of $<0.5\%$. This split ring method benefits from the absence of stress concentrations that may be caused by grips.

The hoop modulus of three types of sections are measured: a ring composed of several layers of tape perfectly stacked in a single tape width around a steel disc and then consolidated in an oven, sections of filament wound tape pipe, as described above, and a pipe made by winding a fabric with tape oriented at $0^\circ/90^\circ$ to the hoop direction. The moduli measured are summarised in Table 7.2.
The laminate equivalent moduli shown in Table 7.2 are defined as follows. The laminate equivalent modulus for the tape ring is based on the tensile modulus of a unidirectional composite processed at the same temperature. The laminate equivalent modulus for the filament wound tape pipe is derived from laminate plate theory based on the properties of a UD plate determined in Chapter 4 of this thesis. A balanced laminate $[+35^\circ_3/-35^\circ_3/0^\circ_2]_s$ is used for comparison since the winding angle of $55^\circ$ is relative to the pipe axis, giving a $\pm 35^\circ$ angle layup in the hoop direction. Due to the asymmetric nature of a $[+35^\circ_3/-35^\circ_3/0^\circ_2]$ laminate, tensile deformation would lead to warping which is not seen in the split disc test. Therefore to provide a laminate equivalent modulus, the modulus of a balanced laminate is calculated using laminate software to provide a closer simulation to the measured hoop modulus of the pipe. The laminate equivalent modulus for the woven fabric pipe is based on the tensile modulus of a woven plate processed at $140^\circ$C and 1.2MPa pressure. This particular laminate was chosen because, even though a compaction pressure was not applied in the creation of the woven fabric pipe, the density of the pipe closely matched the density of the woven plate chosen, and so is seen to be the fairest comparison both in terms of mechanical properties and the presence of interply voids. The ring composed of tapes completely oriented in the hoop direction shows a higher modulus than seen in unidirectional plates investigated in Chapter 4 of this thesis (12.9GPa).
The value measured here is closer to the tensile modulus of the tape (15 GPa), which suggests that the winding of PP tape around a metal disc is a more effective method to constrain All-PP composites, than winding on a flat plate. It is likely that the thermal expansion of the steel disc in heating also provides more effective constraining than the application of lateral pressure.

The filament wound pipe possesses a hoop modulus very close to that predicted by laminate theory. The hoop modulus for this filament wound pipe is much lower than for the unidirectional tape pipe, but this reflects the highly anisotropic properties of All-PP composites ($E_\theta \approx 3$ GPa, Figure 4.9). The hoop modulus of the pipe made from woven tape fabric is very close to the tensile modulus derived from tensile tests. This suggests that the winding of fabrics provides similar constraining in the hoop direction to hot pressing, although the modulus of tapes running in the pipe axis direction, which are not constrained by winding show a higher modulus than expected (4.9 GPa) (Cabrera, 2004). Biaxially oriented PP pipes have been previously reported in literature, although directly die drawing pipes from a tubular billet (Taraiya and Ward, 1991) was limited to an outer hoop draw ratio of $\lambda = 2.3$, so hoop modulus measured (1.54 GPa) is much less than for pipe produced by filament winding of high modulus tapes.

### 7.3.2 All-PP Sandwich Panels

Sandwich panels are composite structures which can possess a very high stiffness to weight ratio. A typical sandwich panel has three components: a thick, low density core with a high shear stiffness and compressive strength, surrounded by two stiff face materials. It can be shown that to create a sandwich panel with optimum bending stiffness per sandwich weight, the weight of the sandwich core should be twice that of both faces (Theulen and Peij, 1991). This is presented in equation 7.1, for a sandwich panel optimised for weight.

\[
W_c = 2W_f
\]

Where

- $W_c = \text{Weight of the core}$
- $W_f = \text{Weight of both faces}$

Since the aim of this research is to produce composite structures in which all phases are polypropylene, sandwich structures are possible that use an All-PP plate as a face material and a PP honeycomb or a PP foam core. It was reported by Allen, 1969, that the bending stiffness of a sandwich panel loaded in four-point bending can be defined by equation 7.2, assuming that $t_f << t_s$, and ignoring local bending stiffnesses.

\[
D = \frac{E_f b t_f (t_f + t_s)^2}{2}
\]

Where

- $D = \text{Bending stiffness of sandwich panel}$
- $E_f = \text{Tensile modulus of face}$
- $b = \text{Width of sandwich}$
- $t_f = \text{Thickness of one face}$
- $t_s = \text{Thickness of panel}$
If this criteria is combined with the optimum weight efficiency criteria, equation 7.1, optimised sandwich panels using All-PP, GMT or Twintex® woven glass/PP faces, and a 80kg.m\(^{-1}\) PP honeycomb core can be compared. The honeycomb used here is produced by Tubus Bauer Gmbh, Germany with a tubular construction, a cell diameter of 8mm and a hexagonal packing arrangement and is representative of a typical PP honeycomb.

Figure 7.8 illustrates equation 7.2, optimised for weight as in equation 7.1. The bending stiffness of the All-PP face sandwich is slightly inferior to woven glass/PP faced sandwich, due to the superior tensile modulus of woven glass/PP. Since the All-PP plate is composed of several plies, the All-PP plates allow much greater flexibility for face thickness, although due to the low density of All-PP plates, the All-PP plate thickness is approximately twice that of the woven glass/PP.

![Figure 7.8. Bending stiffness vs. panel weight of sandwich panels optimised for weight according to equation 7.1](image)

However, the woven glass/PP (in this case, Twintex®) has an areal density of ~750g.m\(^{-2}\) compared to only ~100g.m\(^{-2}\) for plies of woven PP tape. This means that there is a minimum optimum sandwich thickness dictated by the minimum thickness of the woven glass/PP, whereas optimum sandwich panels made with All-PP faces can be made with increments of thickness dictated by the minimum thickness of one ply of fabric (~100g.m\(^{-2}\)) by increasing the number of plies of fabric per face plate. This means that there is much greater design flexibility by using All-PP faces, allowing the production of optimised, lower weight sandwich panels. This simulation has been verified experimentally and is presented in greater detail in a separate thesis (Cabrera, 2004). An All-PP faced PP honeycomb sandwich panel is shown in Figure 7.9.
7.3.3 Thermoforming All-PP Composites

So far in this thesis, no attempt has been made to address forming of All-PP sheets to produce three dimensional shell parts. Thermoforming preconsolidated All-PP plates produced by double belt pressing shows similar results to thermoforming stacked plies of fabric, however, preconsolidated plates are easier to place in a forming mould and may be faster and more economical. If unconsolidated fabrics are used then the thermoforming also should include the application of a minimum compaction pressure to ensure void closure and optimum contact surface between neighbouring plies, as is considered for hot pressing, described in Chapter 4 of this thesis.

Thermoplastic composites, such as GMT, are commonly thermoformed by compression moulding preheated sheets. The moulded plate is then trimmed to remove the excess material around the stamped region. The temperature of stamping glass fibre reinforced PP parts is high enough that the compression induced flow can occur in the mould without bulk flow occurring (Wakeman and Rudd, 2000). In the case of All-PP composites, the temperature of stamping is even more critical, since PP tapes, unlike glass fibres, are highly temperature sensitive. Firstly, preheating of All-PP plates must be done in combination with constraining pressure to prevent shrinkage and loss of mechanical properties prior to stamping. This constraining can be achieved by the use of a clamping frame, which effectively holds the All-PP plate taut during preheating before thermoforming and prevents shrinkage (see Chapter 2). This is simplified by using a preconsolidated All-PP plate since the interply bonding present in the plate assists constraining by the clamping arrangement.

The second concern particular to All-PP composites is the risk of loss of tape properties due to compression induced flow. Since the mechanical properties of the All-PP composite depend on molecular orientation, flow will remove the mechanical properties gained by drawing. However, All-PP composites can also benefit from this temperature dependant behaviour. Figure 5.13 showed that at temperatures above 80°C, the strain to failure increases dramatically. The strain to failure of a single tape at room temperature is shown in Table 7.3.
However, this data refers to a strain rate of \(2.5 \times 10^{-3}\) s\(^{-1}\), and at a typical thermoforming strain rate of \(10^{-1}\) s\(^{-1}\), the strain to failure decreases to \(\approx 50\%\) (Cabrera, 2004) which is still much larger than the strain to failure of glass fibres, 2.6\% (Hull and Clyne, 1996). This increased strain to failure allows drawing during thermoforming which can provide greater complexity in mould design, and also reduces the forming force required. This allows deep drawing with continuous reinforcement, by the elongation of PP tapes, while a woven glass/PP is restricted by the limited strain to failure of the glass fibres. Any additional strain during the drawing of PP tapes is likely to further increase the tensile properties, by further molecular orientation in the drawing direction.

### Table 7.3. Strength and strain to failure of PP tapes, \(\lambda=17\), tested at a strain rate of \(2.5 \times 10^{-3}\) s\(^{-1}\)

<table>
<thead>
<tr>
<th>Test Temperature [(^\circ)C]</th>
<th>Strain to Failure [%]</th>
<th>Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>7.5</td>
<td>450</td>
</tr>
<tr>
<td>100°C</td>
<td>30</td>
<td>290</td>
</tr>
<tr>
<td>120°C</td>
<td>60</td>
<td>175</td>
</tr>
<tr>
<td>140°C</td>
<td>110</td>
<td>100</td>
</tr>
</tbody>
</table>

![Figure 7.10. Thermoforming process of All-PP composites](image)

Figure 7.10 illustrates the thermoforming process. Fabric plies, or a preconsolidated fabric plate (a), are placed in a constraining frame (b) to prevent shrinkage during preheating and also prevent the plate being pulled excessively into the mould during forming. The clamped plate is then preheated in an oven, and then stamped in a cold (40\(^\circ\)C), matched-die mould (c). When the mould is closed, the plate is deformed and also cooled by the total contact with the cold mould. The cool, formed part can then be removed from the mould and the frame (d).

Figure 7.11 shows a hemisphere (radius \(\approx 30\)mm) thermoformed from All-PP plate, by preheating a preconsolidated plate to 140\(^\circ\)C in a matching mould heated to 40\(^\circ\)C. The dominating deformation mode for the forming of woven All-PP plates will be interply shear (e.g. the trellis effect, Figure 6.17) since the modulus of the fabric at \(\pm 45\^\circ\) to the tape direction is much smaller than at \(0^\circ/90^\circ\) (see Figures 4.19, 6.18).

If the copolymer layer between the highly oriented reinforcing phase of the tapes is considered as the bonding medium between fabric plies, it is clear that in addition to increased drawability of the tapes at elevated temperatures, there will also be increased interply shearing due to the softening of the
copolymer component. Thus, a combination of interply shearing and some drawing during forming allows All-PP composites to be readily formed, providing shrinkage and flow is prevented during the preheating or forming stages. A similar effect has been reported for the thermoforming of mono-extruded lower draw ratio PP tape fabrics (Prosser et al., 2000; Harrison et al., 2002).

Figure 7.11. A thermoformed All-PP hemisphere and clamping ring

7.4 Recyclability of All-PP Composites

The original driving force for the creation of All-PP composites was the desire to create composite materials which can compete with conventional composites but have recyclability which is simplified by the use of one material. It is clearly possible to create All-PP composites, but so far it has not been proven that recycling of these composites is possible. Previous studies have shown that isotactic PP can be injection moulded, ground and recycled at least 6 times with a negligible (<10%) change in tensile properties (Aurrekoetxea et al., 2001b, a). A similar study revealed some chain scission and a considerable increase in MFI after extruding and recycling 19 times (Gonzalez-Gonzalez et al., 1998), but this degree of recycling is unlikely to be applied to the recycling of polymers and composites.

Since this establishes that there is only a small effect of thermomechanical recycling on the chemistry of PP, it is necessary to determine the effect of drawability and tape production from recycled All-PP plates. Since the All-PP composites are actually composed of a PP homopolymer blend and a PP copolymer, the effect of recycling these into feedstock must be established. The presence of the PP copolymer can be ignored if the All-PP composite is to be recycled into isotropic products, since commercial recycling of polyolefins into non-structural products typically permits up to 5% non-polyolefin materials (Lankhorst Indutech, 2002). However, when discussing recycling of All-PP composites, it is advantageous to consider recycling All-PP composites back into the feedstock of further All-PP composites. This is desirable from a conceptual point of view as a closed loop recycling process, but also means that waste from tape production, trimming from
formed parts and rejected products can be recycled by granulating and direct reintroduction into extruder feedstock.

To assess the drawability and resulting mechanical properties of tapes containing recycled All-PP granulate, a simple simulation was devised. Since it is not possible to separate co-extruded tape layers into homopolymer and copolymer components, tape or composite granulate can be reintroduced into the homopolymer extruder to become part of the homopolymer core layer. Since this layer is the highly oriented, reinforcement phase of the composite it is crucial that the presence of the recycled copolymer does not reduce drawability or resulting mechanical properties. Since the effect of thermal degradation can be ignored over a small number of cycles, the main interest is the effect of increasing volumes of copolymer in the B layer. To determine this effect, mono-extruded tapes were produced as described in Chapter 2, using the R&D extrusion and two stage post-drawing line at Lankhorst Indutech B.V., The Netherlands.

The tapes were composed of the homopolymer blend used for the production of co-extruded tapes, blended with increasing proportions of copolymer. This simulates the addition of re-granulated composites in the homopolymer core layer; it is the homopolymer core layer in a co-extruded tape that controls the drawability and is responsible for the high mechanical properties of the drawn tape, and so maybe sensitive to this addition. The composition of these tapes is shown in Table 7.4.

**Table 7.4. Mono-extruded tapes created to assess simulated recycling**

<table>
<thead>
<tr>
<th>Tape</th>
<th>Draw Ratio</th>
<th>Tape Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Homopolymer [%]</td>
</tr>
<tr>
<td>V1</td>
<td>13</td>
<td>100</td>
</tr>
<tr>
<td>R2</td>
<td>13</td>
<td>85</td>
</tr>
<tr>
<td>R3</td>
<td>13</td>
<td>70</td>
</tr>
<tr>
<td>R4</td>
<td>13</td>
<td>55</td>
</tr>
</tbody>
</table>

As would be expected for similar polypropylenes, the copolymer and homopolymer successfully mixed and there was no obvious affect on tape extrusion or drawability. The tensile modulus, strength and strain to failure of these tapes was measured as described in Chapter 2. If a co-extruded tape were produced and recycled entirely into the homopolymer core layer of a new tape, a certain proportion of copolymer would be present in the homopolymer core layer, and this proportion would increase with the thickness of the copolymer layer of the original tape and the number of recycles. This proportion of copolymer in the homopolymer core layer can be equated to a number of recycles if the copolymer layer thickness is kept constant. The effect of copolymer being introduced into the homopolymer core layer due to recycling a tape with 11% copolymer (i.e. 5.5% of copolymer on each side of the tape) is shown in Figure 7.12.

It can be seen that after almost 6 simulated recycles, the drawn tapes show a 17% reduction in tensile modulus, a negligible change in tensile strength and a 10% increase in strain to failure. This simulation shows the effect of making new tapes from purely recycled All-PP composites. However, since the waste produced during All-PP composite production is likely to be a small
proportion of the tapes produced, it is more likely that much smaller amounts of tape would be recycled in the feedstock in addition to large proportions of virgin homopolymer.

Since the addition of relatively large amounts of copolymer have a small effect on final tape properties, the addition of very small amounts of re-granulated composite off-cuts or waste tape, to virgin homopolymer may be viable without any significant effect on tape production. However, while the production of tape has been shown to be possible the presence of even small amounts of copolymer in the oriented homopolymer core layer may affect the production and thermal stability of subsequent composites. The presence of coatings such as paints or finishes, mechanical fixings has been ignored in this recycling investigation, so while it has been shown that basic recycling of All-PP composites into new All-PP tapes is possible, it does not address the feasibility of creating new All-PP composites from post-consumer products.

![Figure 7.12. Change in mechanical properties of tape (λ=13) due to simulated recycling](image)

*Figure 7.12. Change in mechanical properties of tape (λ=13) due to simulated recycling*
7.5 Conclusions

The apparent benefits of porosity and reduced density on the specific performance of All-PP composites must be carefully weighed up against problems caused by fluid uptake. This fluid uptake means that even though it is possible to create All-PP composites at a range of pressures, not all pressures are suitable to produce components which are sensitive to water uptake. It is very likely that since the density of All-PP plates increases with compaction temperatures and pressures, water uptake will decrease. Thus, mechanical properties such as maximum specific impact performance, which benefit from low density and poor consolidation, are not suitable if the applications also require minimum water absorption.

Ultimately, the cost of All-PP products depends on the number of processing steps involved and the removal of production rate bottlenecks. By considering processing routes with fewer processing steps, such as filament winding, the cost of the final part can be significantly reduced. The optimisation of the co-extruded tapes is critical, as the wide range of processing routes is made possible by the large temperature processing window achieved by optimising tape production parameters. All-PP products are not limited to tapes, plates and fabrics, as Chapters 1-6 of this thesis may suggest. Careful processing allows the production of pipes, pressure vessels, sandwich panels and three dimensional thermoformed parts.

Since all the parts are composed of All-PP tapes, or a combination of All-PP tapes and bulk PP (such as PP honeycomb, etc) recycling simply requires melting and reprocessing. However, recycling by melting eliminates the economic investment which has been made in the orientation of the molecular structure, by resetting the structure to unoriented state.
Summary

Polymer molecules possess inherent high stiffness. However, the random orientation and coiling of these molecules hugely reduces the modulus of the macrostructure. By orienting the molecules in the same direction, the mechanical properties of the macrostructure can be hugely improved. This orientation can be achieved in a variety of ways for a range of thermoplastics, and this research has focussed on solid state drawing of polypropylene.

Achieving thermoplastic fibres with high mechanical properties by drawing is not new, but it is important to develop a processing method by which these fibres can be exploited as an engineering material. The main obstacle of this processing method is the preservation of the molecular orientation gained by drawing. The consolidation of groups of highly oriented tapes in a unidirectional or bi-directional (woven fabric) form can be achieved by welding the tapes together by heating under pressure. This bonding is achieved while preserving the orientation, by producing the tapes with a low melting temperature skin layer. This skin layer can be melted to bond adjacent tapes, at temperatures below those that risk a loss in mechanical properties of the homopolymer core.

While the modulus of the tapes in this research approaches 50% of the theoretical maximum for the polypropylene crystal, the interlaminar properties of All-PP composites are limited by the weak lateral strength of the tapes, due to the fibrillation and microvoiding caused by high orientation of the tapes. Factors such as tensile modulus, tensile strength, thermal shrinkage, impact resistance and density are all determined by the draw ratio, and these can be explained by considering the microstructure of the tapes.

The aim to produce an engineering material based on a single polymer, polypropylene, has been achieved to satisfy the requirement to generate new materials with a reduced environmental impact. These All-PP composites achieve recyclability since at the end of the product life, an All-PP component can be melted down and recycled into the same component. However, this means the total loss of the processing investment, and since the material cost is very low and the processing investment comparatively large, this may not be straight forward. The reclamation and separation of All-PP products from application, together with the cost of melting may well exceed the low cost of virgin PP. Therefore, even though the potential to recycle is presented by this technology, the incentive to recycle must be supported by legislation, such as the ELV Directive.
References


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