DEVELOPING THE NEXT GENERATION OF POLYETHYLENE BASED SINGLE POLYMER COMPOSITES

A.P.Unwin*, P.J.Hine# and I.M.Ward#

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IRC Meeting September 2009
OUTLINE

• What are self reinforced, single polymer composites.

• Previous studies on polyethylene

• Recent work on polyethylene
   The effect of weave style
   Thermoforming studies
   Production and testing of demonstrator component.
• Composites in which fibres and matrix are both polymers.

• The reinforcing element is usually an oriented polymer fibre or tape, made by drawing to a high level of molecular orientation.

• The term 'Single Polymer Composites' was first coined by Capiati and Porter in their work combining oriented polyethylene filaments with polyethylene powder of a lower melting point.

A variety of processing routes have been proposed for the production of these composite materials:

<table>
<thead>
<tr>
<th>Processing Route</th>
<th>Researchers</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film Stacking</td>
<td>Teishev/Marom and Marais/Feillard</td>
<td>PE</td>
</tr>
<tr>
<td>Bicomponent tapes</td>
<td>Peijs and colleagues</td>
<td>PP</td>
</tr>
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<td>Pressure controlled melting</td>
<td>Marom and colleagues</td>
<td>PE</td>
</tr>
<tr>
<td>Hot Compaction</td>
<td>Hine/Ward</td>
<td>PE/PP/PET/Nylon</td>
</tr>
</tbody>
</table>

Capiati, N. J. and R. S. Porter, "The concept of one polymer composites modelled with high density polyethylene." J.Mat.Sci. 10 (1975) 1671-1677
THE HOT COMPACTION PROCESS

Initial oriented element (fibre or tape) assembly

As the polymer cools, melted material forms a matrix around oriented elements—single polymer composite.

Under pressure and at compaction temperature, surface melting of the individual oriented elements occurs.

Single polymer composite
MELT SPUN POLYETHYLENE

Fibre name: CERTRAN

$M_w$: 130,000

Modulus: 44 GPa


MELT SPUN PE

UNIDIRECTIONAL FIBRES (Certran)

Temperature (°C)

Relative density

% drop in DSC peak

132 134 136 138 140 142 144

0 20 40 60 80 100

50 0.50 0.70 0.90 1.00

Single polymer composites
Very high reinforcement fraction
No impregnation problems
MELT SPUN PE

UNIDIRECTIONAL FIBRES (Certran)

Graph showing the relationship between temperature (°C) and modulus and strength properties of MELT SPUN PE fibres. The graph indicates different trends for longitudinal and transverse properties with temperature changes.
MELT SPUN PE

Morphology and melting behaviour. (DSC) shows two distinct phases.

Aligned PE fibres

Original oriented fibre  Compactated fibres
MELT SPUN PE

Optimum compacted polyethylene fibres - the transcrystalline layer
MELT SPUN PE

Temperature controls oriented phase fraction and hence mechanical properties

![Temperature vs Normalised heat flow graph](image)

- Melted phase
- Oriented phase

Temperature (°C)

- 134°C
- 139°C
- 142°C

Recrystallised matrix phase

Original PE Fibres

Professor David Basset and Dr Robert Olley


POLYPROPYLENE

Woven cloth: Geotextile

\( M_w: 360,000 \)

Modulus: 7GPa

CURV™ - www.curvonline.com
MORPHOLOGY

- Melted and reformed 'matrix'
- Transverse tape
- Oriented tapes
- Melted 'matrix'
- Longitudinal tapes
- Molecular continuity between phases

Compacted woven PP tapes
# MECHANICAL PROPERTIES - PP

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<th>PRELIMINARY DATA (ASTM Standards)</th>
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<td>POOR</td>
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Comparison data for other materials taken from www.matweb.com. Quoted values are averages of all commercially available grades. Compacted PP made on a pilot plant.

CURV™ - www.curvonline.com
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• LIGHTWEIGHT
# MECHANICAL PROPERTIES - PP

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- LIGHTWEIGHT
- MODULUS COMPARABLE TO GMT
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- **LIGHTWEIGHT**
- **MODULUS COMPARABLE TO GMT**
- **OUTSTANDING IMPACT STRENGTH EVEN AT LOW TEMPERATURES**
DEVELOPMENT OF THE HOT COMPACTION TECHNOLOGY

• 1990-1991 INITIAL DISCOVERY
  IRC project 1990-1997

• 1992-1995 INVENTIONS EXTENDED TO MANY FIBRES
  IRC and BTG funding

• 1995-2000 VANTAGE POLYMERS (University Spin-off)
  Initially a joint development project with Hoechst Celanese

• 2000-2009 FULL SCALE COMMERCIALISATION BY BP
  (now with Propex Fabrics Gmbh - Curv™).

• 1999-2009 PARALLEL SCIENTIFIC STUDIES
  EPSRC grant, BTG funding,
  BP funding, DTI funding
COMMERCIALISATION

Hot compacted PP (Curv) successfully commercialised by Propex Fabrics (formerly BP)

Wilson Benesch Loudspeakers
Nike: Contour BPS Soccer shinguard
Samsonite X-Lite luggage range
Automotive undertray

www.curvonline.com
COMMERCIALISATION

- Nike BP Contour BPS
- Protective case - violin
- Kiteboard
- Automotive undertray
- Sandwich panel
- Protective case - laptop
- Automotive undertray
A commercial application for hot compacted PP sheet (CURV™) is for NIKE soccer shinguards (Contour BPS).

The picture on the left shows hot compacted/foam PP shinguards which are now on the market.
The combination of high impact strength, even at low temperatures, and good abrasion resistance, makes hot compacted PP an ideal material for under body shields.
AUTOMOTIVE APPLICATIONS

<table>
<thead>
<tr>
<th></th>
<th>Hot Compacted PP</th>
<th>GMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>900 gms</td>
<td>1200 gms</td>
</tr>
<tr>
<td>Puncture impact</td>
<td>14.5 J</td>
<td>9.6 J</td>
</tr>
<tr>
<td>energy @ + 20°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Puncture impact</td>
<td>14.1 J</td>
<td>10.5 J</td>
</tr>
<tr>
<td>energy @ - 40°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notched Izod</td>
<td>4750 J/m</td>
<td>750 J/m</td>
</tr>
<tr>
<td>@ + 20°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Notched Izod</td>
<td>7500 J/m</td>
<td>Brittle</td>
</tr>
<tr>
<td>@ - 40°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abrasion resistance</td>
<td>&gt; 3 hours</td>
<td>1 hour 40 mins</td>
</tr>
</tbody>
</table>

- CURV™ thermoformed undershield out performed GMT on all mechanical property requirements.
LUGGAGE

Samsonite suitcase (X-Lite range) from Curv™
Joaquín Cortés

"I consider myself a nomad of the twenty-first century, though as a good Gypsy obviously I travel by plane. Before the Gypsies traveled in covered wagons with their cattle and horses. Now things have changed. I look at myself as an ambassador of my country and my culture."

The X'Lite Collection

The lightest and strongest luggage Samsonite has ever created. Its distinction is in its unique construction. Made with the exclusive CURV® material — layers of woven synthetic fabric formed into self-reinforced, composite sheets — for the traveler who wants easy luxury with an edge.

tour the collection

about joaquin

travel tips
FUTURE STUDIES

ADVANTAGES

• Lightweight
• Good mechanical properties
• Thermoformable
• High impact performance
• Recyclable

DISADVANTAGES

• Stiffness drops with increasing strain
• Stiffness drops with increasing temperature
• Poor creep resistance at elevated temperatures (target 120°C)
• High thermal expansion

Nike Contour BPS shinguard

Automotive undershield
The aim is to develop the next generation of self-reinforced polymer composites.

Key Targets

- Reduce the amount of plastic used to make a component by 30%.
- Reduce component weight by 30%.
- Improve the recyclability of reinforced plastics.
- Improve the design flexibility of self-reinforced plastics.
The project involves 8 UK partners representing the entire supply chain.
## RECENT PE RESEARCH

<table>
<thead>
<tr>
<th>Fibre name:</th>
<th>CERTRAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$:</td>
<td>130,000</td>
</tr>
<tr>
<td>Modulus:</td>
<td>44 GPa</td>
</tr>
</tbody>
</table>

- Futureplas studies used the same PE fibre as the original hot compaction work.
- Two weave styles available:
  - Plain weave
  - Unidirectional weave made specially by James Dewhurst

Unidirectional cloth

Plain weave

![Unidirectional cloth](image1.png)

![Plain weave](image2.png)

PET carrier, low crimp but difficult to handle

Balanced, conformable, high crimp.
A woven fabric is normally used to give balanced properties in the final single polymer composite.

If the surface of the woven fabric is rough, then more matrix material is required to bond the layers (~30% melted material) than between the fibres in each bundle (~10% only).

This can require a compaction temperature close to the point where the whole crystalline structure melts.

Using an interleaved film allows a lower compaction temperature to be used, thereby widening the processing window and increasing interlayer bonding (which can be crucial for thermoforming).
RECENT PE RESEARCH

Unidirectional cloth - 0/90 configuration
Made with and without an interleaved film

- No significant effect on modulus with the introduction of an interleaved film.
- Balanced unidirectional weave gives a higher modulus compared to a high crimp plain weave (previous research showed a tensile modulus of 10GPa for a plain weave sample made without film).
Unidirectional cloth - 0/90 configuration
Made with and without an interleaved film

Samples 350mm x 300mm

- Similar results for strength.
- Strength drops rapidly for a compaction temperature > 140.5°C
RECENT PE RESEARCH

Unidirectional cloth - 0/90 configuration
Made with and without an interleaved film

- Peel strength higher with interleaved film and less sensitive to compaction temperature.
- The optimum temperature is therefore ~139°C with a film - good stiffness and strength but not risking significant fall in stiffness or strength with hot spots in processing (i.e. wider processing window). Samples can be made without film if preferred at ~140°C.
A comparison of properties tested in tension and bending

<table>
<thead>
<tr>
<th>Weave Style</th>
<th>Test Type</th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uni (0/90) + film</td>
<td>Tensile</td>
<td>20</td>
<td>250</td>
</tr>
<tr>
<td>Uni (0/90) + film</td>
<td>Flexural</td>
<td>22</td>
<td>69</td>
</tr>
<tr>
<td>Plain + film</td>
<td>Flexural</td>
<td>9.4</td>
<td>68</td>
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- Typical properties at the optimum compaction temperature of 139°C.
- The Unidirectional weave style (0/90) showed twice the stiffness of the plain weave style due to less crimp.
- The flexural strength was found to be significantly lower than the tensile strength and independent of weave style.
Hot tensile tests - UD 0/90 with film

• Hot tensile behaviour quite different to previous work on PP.
• For PE, after yielding there is very little resistance to stretching.
• Stress (resistance to stretching) falls with post forming temperature.
• Maximum failure strain at 100°C (for PP the failure strain increased with post forming temperature).
For PP the strain to failure increases with temperature making it an advantage to get close to the melting point.

For PE the strain to failure goes through a maximum and then falls significantly with temperature making it an advantage to be at a lower temperature for forming.
Hot tensile tests – all weave styles

100°C is a good choice for the post forming temperature as the failure strain passes through a maximum at this point for all weave styles.
Thermoforming

Hemispherical Mould

- Hemispherical tool installed in an environmental chamber.
- Sheets were thermoformed for a range of temperatures, closing speeds and gripping arrangements.
- Excellent hemispheres made from both weave styles. The best samples were made at ~100°C, correlating well with the hot tensile tests. At higher temperatures the sheet was seen to tear on forming and at lower temperatures the sheet was difficult to form.

Hemisphere from the unidirectional sheet (note the PET carrier): formed at 100°C
RECENT PE RESEARCH

Thermoforming of a demonstrator component

- Centre Console Bracket (part and matched metal tooling) supplied by Visteon.
- The aim is to evaluate the mechanical properties of a lighter weight thermoformed polymer/polymer composite in an application typically fabricated from a steel stamping.
Thermoforming of a demonstrator component

- Simple component
- Plain weave
- no film

- Matched tooling installed on tensile test machine.
- Mould heating by an air gun: samples heated in an oven (120°C).
Thermoforming of a demonstrator component

- 2 stage procedure: close the mould at 200mm/min to 10kN, compress the sheet at 10mm/min into 100kN.
Recent PE Research

- Trimmed and drilled to produce comparison with metal part.
- Metal part weight 115g  PE part weight 20g
Thermoformed samples were subjected to mechanical loading to simulate bracket function.
Test Specification: Strength and Rigidity:
Application requires bracket to be free of damage and permanent deformation on application of a load of 500N.

- No change in stress-strain behaviour after three applications of 500N at 20°C.
Test Specification: Strength and Rigidity:
Application requires bracket to be free of damage and permanent deformation on application of a load of 500N after spending 7 days at 80°C or spending 4 hours at 105°C.

- No change in stress-strain behaviour after 7 days at 80°C

Small reduction in stiffness after 4 hours at 105°C
Test Specification: test to destruction

- Does not fracture, but buckles. Could be an advantage for this application.
CONCLUSIONS

- An interleaved film widens the processing window and improves interlayer strength.

- A unidirectional weave style gives twice the sheet stiffness and strength compared to a plain weave.

- The flexural strength is much lower than the tensile strength and independent of weave style.

- The best thermoforming temperature is 100°C. At higher temperatures, the resistance to forming decreases, but so does the strain to failure.

- A demonstrator component was successfully thermoformed using matched metal tooling from hot compacted PE sheet. The single polyethylene composite part weighed one fifth of the equivalent metal part and has passed the specified test.
ACKNOWLEDGEMENTS

• FuturePlas colleagues.

The Futureplas project is co-funded by the Technology Strategy Board’s Collaborative Research and Development programme, following an open competition. The Technology Strategy Board is an executive body established by the Government to drive innovation. It promotes and invests in research, development and the exploitation of science, technology and new ideas for the benefit of business - increasing sustainable economic growth in the UK and improving quality of life.
ACKNOWLEDGEMENTS

• Ian Ward and Keith Norris
• Derek Riley
• Mark Bonner, Glen Thompson and co-workers
• David Bassett, Robert Olley and co-workers
• British Technology Group
• Hoechst Celanese
• BP (BP Amoco Fabrics Gmbh), Propex Fabrics
WHY SINGLE POLYMER COMPOSITES?

- Lightweight.
- Recyclable (no glass fibres).
- Thermoformable.
- Lower energy consumption when making parts.
- Outstanding impact: ductile under all conditions.
- Forms a bridge between isotropic and glass filled polymers.
- Enhanced properties compared to isotropic PP at the same density.
- Versatility of isotropic PP with the properties of fibre reinforced PP (GMT).
 Other Polymers

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<th>PP</th>
<th>PET</th>
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<td>11</td>
<td>14</td>
<td>5.8</td>
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<tr>
<td>Matrix modulus (GPa)</td>
<td>0.5</td>
<td>1.2</td>
<td>2.8</td>
<td>1.9</td>
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<tr>
<td>Initial sheet modulus</td>
<td>30</td>
<td>5</td>
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![Graphs showing stress-strain and DNA thermal modulus for various polymers]