EXECUTING TRANSFORMATION AND INVESTING IN GROWTH
New Materials & New Processes for the 2020s: Additive Manufacturing

Tecnon OrbiChem Knowledge Partners’ Seminar at GPCA 2018
Dubai, 26 November 2018

Gillian Tweddle – Business Manager, Individual Project Studies
OUR CORE STRENGTHS
Intermediates, Fibres & Specialty Resins
WHAT IS ADDITIVE MANUFACTURING?

Additive Manufacturing, often called 3D Printing, is a technique for producing solid objects, often intricate in shape, by arranging particles in space under computer control, with a method for fusing the particles together.

The particles can be made of:

- Plastics materials
- Silicones
- Metals
- Ceramics

Objects are built up layer by layer.

An alternative method is to use successive layers of photo-sensitive liquid that can be polymerised in shapes determined by directed UV light beams.

Source: Tecnon OrbiChem
ADDITIVE MANUFACTURING – WHY SHOULD WE BE INTERESTED?

• What is the current situation and prognosis for the future?
• To what extent will AM become increasingly important as a destination for polymers produced by plastics manufacturers?
• What are the opportunities for polymer manufacturers to add value to engineering polymers by generating more specialised grades with increased technical service?
• Engineering polymer producers are interested in participating in this relatively new industry to gain experience, and be in a position to participate in expected future larger markets.

Source: Tecnon OrbiChem
There are several techniques whereby plastics materials in minute packets can be arranged spatially and polymerised and/or bonded together. The main ones are:

**Techniques Used in Additive Manufacturing**

- **Selective Laser Sintering - SLS**
  - Use **powders** that can be instantly bonded together after placement.

- **Multi Jet Fusion (MJF)**
  - Use **powders** that can be instantly bonded together after placement.

- **Fused Filament Fabrication - FFF**
  - Use thermoplastic **solid** polymers that are melted, extruded to a nozzle unit and deposited to form layers.

- **Stereo Lithography - SLA**
  - Use a **liquid** prepolymer, which a UV light or laser beam causes to polymerise at spatial points.

- **Polyjet**
  - Use **liquid** prepolymer, which a UV light or laser beam causes to polymerise at spatial points.

Various methods are used to get the particles to bind together:
- Molten materials can be allowed to congeal.
- UV-sensitive additives are added to plastic material, which is photo-cured by UV light.
- Powders are melted in situ with lasers or infrared heat on fusing agents.
- Liquids can be vulcanised.

Source: Tecnon OrbiChem
Commonly used plastics materials:

- ABS
- Polylactic acid (PLA)
- Polypropylene
- Polyamide 6
- Polyamide 6 + 66 blend
- Polyamides 11, 12
- Epoxy resin
- Polystyrene
- Wood flour + PLA

Less widely used materials:

- HDPE
- Polycarbonate
- PETG
- Polyvinyl alcohol (PVA)
- PPS
- Acrylics
- PEEK
- Silicones and Rubbers
- Chocolate!

Various reinforcements and additives can be incorporated in the polymer. Carbon or glass fibre is used to increase the rigidity and strength of the final article. Ceramic particles help in heat induced post-curing. Addition of graphene enables electrically conducting articles to be formed.

Source: Tecnon OrbiChem
**LIQUID AM : STEREO-LITHOGRAPHY (SLA)**

- Stereolithography (SLA) converts liquid materials into solid parts, layer by layer, by curing them via photo-polymerization using a UV light source. SLA uses a liquid pre-polymer, consisting of low molecular weight oligomers, to which has been added a photo initiator. When the prepolymer is exposed to UV light from a laser, the photoinitiator molecule breaks down into radicals, which interact with the active groups on the oligomer chains, which then react with other active groups, forming longer chains. As the chains lengthen and cross-link, the resin solidifies, which all happens in milliseconds.

- SLA is an example of a solid object being created in a bath of liquid, a process called vat photopolymerisation.

- Photopolymer resins are thermosetting plastics. Polymerisation may need to be completed with subsequent UV or heat curing.

- SLA is comparatively rapid, and produces parts with good surface finish in high resolution.

Source: Tecnon OrbiChem
The Polyjet process uses liquid photopolymers, which are fed to a head on a carriage, which operates like an ink-jet printer. The inkjet head has several hundred nozzles. Droplets are jetted on to a surface and are then cured by UV light. After a thin layer is created, the process repeats itself by jetting additional layers until the part is fully formed.

Polyjet printing is more precise and has smoother surfaces than FDM printing. It is good for printing small, intricate parts or artistic projects where surface finish is important. However, polyjet parts can be brittle, so are not suitable for mechanically demanding applications.

Polyjet printers can mix 2 or 3 resins during printing, so parts can be made with different materials for different levels of flexibility or transparency.

Polyjet is unique among AM printers in being able to use rubber-like resins in addition to rigid resins.

The main polymers (liquid) used for Polyjet are:
- Acrylics
- Silicons, of Shore hardness 30-95

Source: Tecnon OrbiChem
SOLID: FUSED FILAMENT FABRICATION (FFF)

- Fused filament fabrication (FFF) uses a continuous filament of a thermoplastic material, which is fed from a large coil, through a moving, heated, printer extruder head. Molten material is forced out of the print head's nozzle and is deposited on a workpiece that grows, layer by layer. The head is moved, under computer control, to define the printed shape.
- Layers can be bonded together by temperature control, or by adhesives.
- FFF is often referred to as Fused Deposition Modelling (FDM), which however is a trademark of Stratasys Inc. FFF is the most widely used industrial system. On the other hand it is suitable for small scale equipment, used even in Do-it-yourself printers.
- Speed is low compared to other AM processes, and accuracy is limited by the size of the printer head nozzle.
- In a variation called Continuous Filament Fabrication (CFF), printers use a second nozzle to lay continuous strands of carbon fibre etc., to produce a reinforced object of considerable strength.

The main polymers (solid) used for FFF are:
- ABS
- ABSi (translucent)
- PLA
- Polycarbonate
- Polyamide
- Polystyrene
- Polyphenylsulphone
- PETG

Source: Tecnon OrbiChem
SOLID: SELECTIVE LASER SINTERING (SLS)

- SLS is an example of a Powder Bed Fusion process.
- SLS machines take a powder, usually of a plastics material, and disperse it in a thin layer on top of the build platform. A CO2 laser pulses down on the platform, tracing a cross-section of the object onto the powder. The laser heats the powder to just below its melting point (sintering) which fuses the particles together into a solid form. The platform of the SLS machine then drops, exposing a new layer of powder for the laser to trace and fuse together. This process continues repeatedly until the entire object has been printed. Excess powder is then removed.
- Unlike other methods of 3D printing, SLS objects do not usually have to be sanded or otherwise altered once they come out of the SLS machine.
- A similar process is Selective Laser Melting, in which the powder is heated above its melting point. Properties of the final object are different.

The main polymers (solid) used for SLS are:

- Polyamide 12
- Polyamide 11

They can be unfilled, or mineral or glass fibre filled.

Various metals can be used in similar processes called Direct Metal Laser Sintering (DMLS).

Source: Tecnon OrbiChem
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SOLID: MULTI JET FUSION (MJF)

• MJF was introduced 3 years ago by HP. It is similar to SLS but uses infra-red heating rather than pulsed laser radiation.

• MJF is a powder-based technology that uses a heated powder bed. A fusing agent is jetted where particles need to be selectively melted, and a detailing agent is jetted around the contours to improve part resolution. As IR lamps pass over the surface of the powder bed, the jetted material captures the heat and helps distribute it evenly.

• MJF uses a fine-grained PA 12 material that allows for ultra-thin layers of 80 microns. This leads to parts with high density and low porosity, compared to PA 12 parts produced with Laser Sintering. It also leads to an exceptionally smooth surface straight out of the printer, and functional parts that need minimal finishing. That means short lead times, ideal for functional prototypes and small series of end parts.

Source: Tecnon OrbiChem
Selective Laser Sintering can function with many materials, but only a limited number are commercially available, indicated in blue in the “pyramid of polymeric materials”.

Materials indicated in orange are mentioned in research, but are not supplied as powders for SLS. Some elastomers are usable.

PA12 is the most widely used material for SLS, having ideal melting point, mechanical properties and water uptake. PA11 is a cheaper alternative but has poorer dimensional stability.

Amorphous polymers generally create objects whose porosity is too high.

DOI: 10.1021/acs.chemrev.7b00074

Source: Tecnon OrbiChem
<table>
<thead>
<tr>
<th>Polymers for AM (1) - General Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ABS</strong></td>
</tr>
<tr>
<td>- ABS is the polymer in most widespread used in AM, as it provides easy processing, low warpage, and a tough and impact resistant product with good print surface quality.</td>
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<tr>
<td>- Printing temperature 230–260°C.</td>
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<tr>
<td>- A standard polymer for FFF/FDM processing. Liquid form used in SLA and Polyjet processes.</td>
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<tr>
<td><strong>Polylactic Acid</strong></td>
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<tr>
<td>- Made from renewable resources and biodegrades, so a popular choice. Parts made from it are brittle, but can be improved with additives.</td>
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<tr>
<td>- Printing temperature of 190°C permits sharper details than ABS, but end parts are not suitable for use above 60°C.</td>
</tr>
<tr>
<td>- Preferred material for low cost FFF printers.</td>
</tr>
<tr>
<td><strong>Polyvinyl Alcohol</strong></td>
</tr>
<tr>
<td>- The main feature of PVA is that it dissolves in water. It is used in a 3D printer to form supports around an object being printed in ABS, PLA, etc. The supports allow objects to be printed that are complex, or even with movable parts. The supports can later be dissolved away.</td>
</tr>
<tr>
<td>- Printing temperature 200°C.</td>
</tr>
<tr>
<td>- Used in FFF printers with multiple extruders.</td>
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</tbody>
</table>

Source: Tecnon OrbiChem
**Polycarbonate**
- High impact resistance and relatively high heat resistance make PC an excellent choice for making functioning prototypes, especially where transparency and non-conductivity are desired.
- Printing temperature of 200ºC is needed.

**Polyamide 6 and 66**
- PA6 is tough and has high tensile strength, so is preferred for high performance machine parts to industrial applications including automotive and aerospace. PA66 is similar but with higher heat resistance.
- Printing temperature 250ºC for PA6, 280ºC for PA66.
- Popular for use as filaments in FFF/FDM processing, due to low cost and high end part mechanical properties.

**Polyamide 12**
- PA12 is a specialised material, that has a special role to play in AM. It is an ideal material for use in SLS printing, and is the only material that can be used for MJF.
- Printing temperature 184ºC.
- Due to its molecular structure, PA12 has an almost unique set of mechanical properties resulting from interlayer bonding of successively sintered layers, that reduces anisotropy. Also used in FFF printers.

Source: Tecnon OrbiChem
**GPCA 2018**  
**POLYMERS FOR AM (3) - CHALLENGING METALS**

<table>
<thead>
<tr>
<th><strong>PEEK</strong></th>
<th><strong>Polyetherimide</strong></th>
<th><strong>Various</strong></th>
</tr>
</thead>
</table>
| • PEEK (polyetheretherketone) is part of the PAEK family (polyaryletherketone). It shows high mechanical performance and exceptional resistance to high temperatures. Applications in the fields of aeronautics and aerospace.  
• It requires extreme printing parameters: an extrusion temperature of more than 350° C, a heated chamber and a printing bed capable of rising to more than 100°C. | • PEI is used for demanding applications that require high heat resistance, high strength, high modulus, low creep and low flame, smoke and toxicity.  
• Printing temperature of 230°C is needed.  
• Easier to print than PEEK, used where lower usable temperature and impact strength are acceptable, and lower cost desirable. | • Many other high performance polymers are capable of 3D printing, including:  
• Polyphenyl ether (PPE)  
• Polyphenyl sulphone (PPSU)  
• Polybutylene terephthalate  
• Polyetherketoneketone  
• Alumides (polyamide +aluminium powder) |

Source: Tecnon OrbiChem
UK-based engineering solutions provider, KW Special Products, is leading a project to create a ‘while you wait’ service for personalised 3D printed insoles. KWSP, with Newcastle University and advanced foot orthotics manufacturer, Podflo Ltd., aims to create a printing process for insoles by early 2019.

The aim is to develop equipment that allows clinicians to take a patient’s individual sole measurements, create a prescription design, and 3D print a custom orthotic on-site, reducing the current time taken to produce insoles.

Source: Tecnon OrbiChem
Adidas began shipping its Futurecraft athletic shoes, that use a 3D-printed mid sole, in January 2018. Adidas intends to make 100,000 Futurecraft shoes during 2018.

The Futurecraft sole is the result of a collaboration between Adidas and Carbon, a Silicon Valley startup company. Carbon has developed a 3D printing process using a liquid polymer resin that is cross-linked and solidified by UV light. This process could be the breakthrough in 3D printing that ushers in mass manufacturing, making it sufficiently fast, cheap, efficient and reliable.

Source: Tecnon OrbiChem
• Demand for 3D printed items now comes from a number of opportunities:
  o Prototyping of individual components
e.g. for the aerospace or automotive industry
  o Limited production runs, avoid the need for tooling such as for injection moulding or extrusion e.g. concept vehicles
  o For ‘high end’ applications where the component cannot be readily manufactured using existing techniques
  o Mass customisation: orthopaedic shoe soles, dental implants and hearing aids
  o Spare parts manufacture on an “as needed” basis reducing or eliminating need for stock

• Overall demand and demand for engineering polymers is currently small but is expected to grow strongly as demand moves to the ‘early adopters’ phase of the product adoption curve.

• Some applications are considered “commercial” rather than simply the preserve of “tech enthusiasts”

• Co-operations between plastics makers, filament/powder/liquid producers 3D printer makers and end customers are required because printing techniques and machines differ and a high level of customisation is required for each application.

• Existing engineering plastics grades for injection moulding provide a start point for new grades with a high level of technical service as a key component of the product

Source: Tecnon OrbiChem
CONCLUSIONS

• There is a wide range of 3D printers available, with widely differing capabilities.
• Some 3D printers are suitable only for small production runs, e.g. to create prototypes, but new types are emerging that hold promise for mass production.
• Some printer types can use only specific plastics materials, others are versatile. In general existing engineering polymers need to be adapted for 3D printing applications.
• The industry is served by many small enterprises that supply the specialised polymer types in the requisite filament powder or photo-sensitive liquid form.
• The large commodity plastics manufacturers are starting to take an interest in AM, seeing the potential for its emergence as a mass manufacturing activity.
• The ability to manufacture in mass, but with each printed object tailor-made to the individual customer, promises a revolution in made-to-order retailing.
• Low investment costs offer inexpensive entry to small enterprises aiming at plastics processing.

Source: Tecnon OrbiChem
New Materials & New Processes for the 2020s: Composites Manufacturing

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Matthew Hartley - Senior Consultant, Individual Project Studies
OUR CORE STRENGTHS
Intermediates, Fibres & Specialty Resins

- Soda Ash
- Caustic Soda
- Chlorine
- Derivatives
  - EDC
  - Acetic Acid
  - Vinyl Acetate Monomer
- Isocyanates
- Peroxy PO
- Chlorohydrin PO
- Ethylene Oxide
- EO Derivatives
- Polyols
- Caprolactam
- AH Salt
- Paraxylene
- Adiponitrile
- Adipic Acid
- Methanol
- Acrylic Acid
- Methyl Acrylate
- Ethyl Acrylate
- 2-Ethylhexyl Acrylate
- Butyl Acrylate
- Isodecanol
- Isononanol
- 2-PH
- 2-EH
- DOP
- DIDP
- DINP
- DPHP
- Orthoxylene
- Phthalic Anhydride
- Unsaturated Polyester Resin
- Maleic Anhydride
- 1,4-Butanediol
- Styrene
- Acetone
- Phenol
- Bio-Materials
- Polyester Fibre
- Polyamide Fibre
- Polyester Film
- Polyurethanes
- Polyester
- Polypropylene Fibre
- Polyamide 6
- Polyamide 66
- Polyamide Resin
- Polyacetal
- ABS & SAN
- PBT
- Polycarbonate
- Polyethylene
- PVC
- Epichlorohydrin
- Epoxy Resins
- Bisphenol A
- Polyurethanes
- Polyester
- Polyethylene
- Acrylic Fibre
- Acrylonitrile
- Polyamide 6
- Polyamide 66
- Polyamide Resin
- Polyacetal
- ABS & SAN
- PBT
- Polycarbonate
- Polyethylene
WHAT IS A COMPOSITE?

A multiphase material formed from a combination of materials which differ in composition, remain bonded together, and retain their identity and properties.

The components act in concert to provide improved properties not obtainable from one of the original components acting alone.

Types of composites include:

• Fibres embedded in a matrix
• Layers of materials
• Particles or flakes in a matrix
• Combinations of the above

The most widely known are Polymer Matrix Composites, which are a synergic combination of high performance fibres within a polymer matrix. The fibre provides the high strength, while the polymer spreads the load and provides resistance to weathering and corrosion.

Source: Tecnon OrbiChem
Thermosetting polymers permit great versatility in forming the reinforced article to the right shape and with optimum distribution of strength and stress resistance. Fabrication can be undertaken at room temperature, with low viscosity helping penetration of fibre mats, while curing (involving cross linking of molecules) can be chosen to take place between 0 ºC to 200 ºC according to the nature of the polymer and curing agent.

Best known thermosetting polymers include:

• Unsaturated polyester resins : MPG + PAn + MAn; Styrene solvent; Peroxide activator
• Vinyl esters : Epoxide resin + Methacrylic acid; Styrene solvent; Peroxide activator
• Epoxy resins : Bisphenol A + Epichlorohydrin; Curing agent (cross-linker)

These are in order of increasing physical properties but also cost. The choice between them often depends on whether the improved properties are justified by the extra cost.

Source: Tecnon OrbiChem
Thermoplastic polymers are melt processed. They are shaped at a temperature high enough to make them soft or liquid and then retain the shape on cooling. Clearly the final article can be used only in applications where the operating temperature stays well below the softening point. This is their weakness compared to thermosets, but they have advantages of:

- Defined and reproducible mechanical properties
- High impact strength and fatigue resistance
- Recyclability
- Infinite shelf life
- Rapid production cycles – the key to adoption in the automobile industry

But thermoplastics have been held back, compared to thermosets, by their limitation to reinforcement by short fibres, up to 6 mm in length.

However, that has been changing rapidly in recent years.

Source: Tecnon OrbiChem
Long fibre reinforced thermoplastics (LFRT) have become available as pellets that are used in injection moulding and compression moulding. This brings enhanced mechanical properties and weight reduction to the moulded article, while permitting fast moulding. Automobile manufacturers want cycle times of 90-120 seconds, which can be met by thermoplastics, but not easily with thermosets.

Unlike thermosets, thermoplastic parts can be combined together by heat, sonic or induction welding. This eliminates the need for adhesives or fasteners, as must be used with thermosets.

Source: Tecnon OrbiChem
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**THERMOPLASTIC IN COMPOSITES**

Common Thermoplastic + Fibre Composites

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass</th>
<th>Carbon</th>
<th>Aramid</th>
<th>Steel</th>
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<tbody>
<tr>
<td><strong>Commodity Plastics</strong></td>
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<td>PLA</td>
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<td>HDPE</td>
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<td>PET</td>
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<td>Polycarbonate</td>
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<td>ABS</td>
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<td>TPU</td>
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<td>Polypropylene</td>
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<tr>
<td>Polyamide 6 &amp; 66</td>
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<tr>
<td><strong>High Performance Polymers</strong></td>
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<tr>
<td>Polyphenylene Sulphide</td>
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<tr>
<td>Polyether Ether Ketone</td>
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<td>Polysulphone</td>
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<tr>
<td>Polyetherimide</td>
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</tr>
</tbody>
</table>

§ Preferred for continuous filament reinforced thermoplastic
‡ Preferred for aerospace applications

Source: Tecnon OrbiChem
Arevo’s technology combines 3-D printing with web-based software and customised raw materials. This bike was taken from concept to rideable production in less than 18 days – and it weighs only 13 lbs.

Source: Arevo Inc.
Continuous fibre reinforced thermoplastics (CFRT) come in the form of **unidirectional tapes**. Filament is also used for woven sheets, filament winding and pultrusion. These techniques permit more complex designs than with thermosets or metals.
The BMW i8 Coupé is exceptionally lightweight. It is built from an aluminium chassis and an ultralight passenger compartment made of high-strength carbon-fibre reinforced composite.
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COMPOSITES TAKE ON DEMANDING TASKS

Source: Carbon Revolution
• The Boeing 787 (right) was the first major commercial airplane to have a composite fuselage, composite wings, and use composites in most other airframe components. Each 787 contains approximately 35 tons of CFRP, made with 23 tons of carbon fibre.

• The wings of Airbus’s A350 are made more than 50% of carbon fibre reinforced plastic. Pilots can move flaps while cruising to boost efficiency during various phases of the flight.
NASA has asked Made In Space Inc., CA, USA, for a proposal for a technology flight demonstration mission of its Archinaut technology.

Archinaut is an in-space robotic additive manufacturing and assembly platform capable of constructing objects in space stations. The absence of gravity enables manufacturing of large structures. The equipment uses high-strength space-grade polymers, such as PEI/PC ULTEM (polyetherimide/polycarbonate).
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COMPOSITES IN ARCHITECTURE

The San Francisco Museum of Modern Art
A team of students from Cornell University won first place in a competition to develop a composite architectural/building component or assembly. The winning design was “Tubular Knitting” – a lightweight, spatial and structural tube that can serve as an alternative for a column.
Are epoxies or polyurethanes the polymers that will prevail as blade lengths start to exceed 100 metres in length?
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