POLYMERS IN ADDITIVE MANUFACTURING

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MARKET SEGMENTED BY MATERIAL TYPE (2015)

- Photopolymers: 45.5%
- LS polymer powders: 24.9%
- Filaments: 11.5%
- Metals: 3.1%
- Others: 15.1%

Source: Wohlers Associates, Inc
MARKET FOR POLYMER MATERIALS

Fast growing market for polymer materials
- $150M in 2005, $850M in 2015, $6,200m in 2025
- Annual growth ~25%

Slow decrease of the average cost of polymer materials
- From $270/kg in 2014 to $220/kg in 2025

Source: SmartechMarkets 2015
INDUSTRIAL PRODUCTION

COST EFFECTIVE FOR SMALL SERIES

Costs per part (€)

Number of Parts

Additive Manufacturing
Injection Molding
MAIN POLYMERIC FAMILIES

- Automotive
  - (ABS, PA)

- Aeronautic
  - (PA, PEI, PEKK, PEEK)

- Sport
  - (PA, TPU, Photopolymers)

- Consumer products
  - (ABS, PLA, Photopolymers)

- Electronic
  - (Photopolymers)

- …

Air duct for laminar flow
Source: EOS

Aircraft fitting before and after structural shape optimization
Source: Oxford Performance Materials
# MARKETS AND APPLICATIONS FOR POLYMER 3D PRINTING

## Industry

<table>
<thead>
<tr>
<th>Industry</th>
<th>Current Applications</th>
<th>Future Target Applications</th>
<th>3D Printing Technologies</th>
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<tbody>
<tr>
<td><strong>AEROSPACE</strong></td>
<td>Non critical cabin and structural components, assembly tooling</td>
<td>Structural components, high volume cabin components</td>
<td>SLS, material extrusion</td>
</tr>
<tr>
<td><strong>AUTOMOTIVE</strong></td>
<td>Prototypes, assembly tooling, functional test parts for concept cars</td>
<td>Interior components, customized parts for product differentiation</td>
<td>SLS, material extrusion, SLA, material jetting</td>
</tr>
<tr>
<td><strong>CONSUMER PRODUCTS</strong></td>
<td>Models, prototypes, custom low complexity products</td>
<td>On-demand consumer products and end use components</td>
<td>SLA, material jetting, binder jetting,</td>
</tr>
<tr>
<td><strong>MEDICAL</strong></td>
<td>Anatomical models, surgical tools and guides, implants, upper extremity prosthetics</td>
<td>High realism and multi material models, load bearing implants, lower extremity prosthetics</td>
<td>SLA, SLS, Material jetting</td>
</tr>
</tbody>
</table>
3D TECHNOLOGIES USING POLYMERS

MATERIAL EXTRUSION
(Fused Deposition Modeling, FDM)
- Thermoplastic polymers filaments
- Parts with good mechanical properties and durability

POWDER BED FUSION
(Selective Laser Sintering, SLS)
- Thermoplastic polymer powders
- Parts with good mechanical properties and durability

VAT PHOTOPOLYMERIZATION
(Stereolithography, SLA)
- Photocured polymers
- Good surface finishing

MATERIAL JETTING
(PolyJet, MultiJet)
- Photocured polymers
- Multimaterial, multicolor
LASER SINTERING WITH HIGH TEMPERATURE POLYMERS

PEKK - POLY(ETHER KETONE KETONE)

PEKK has unique features
- More Ketone links for higher Tg (160°C) and higher strength (Tens. 110MPa, Comp. 145MPa)
- It is a copolymer, offering control over Tm (305, 330, 360°C) and crystallization rates

### GRADES KEPLAN

<table>
<thead>
<tr>
<th>Grades</th>
<th>Type</th>
<th>T/I Ratio</th>
<th>Tg</th>
<th>Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>8000 Series</td>
<td>Semi-crystalline</td>
<td>T/I = 80/20</td>
<td>Tg = 165°C</td>
<td>Tm = 358°C</td>
</tr>
<tr>
<td>7000 Series</td>
<td>Semi-crystalline</td>
<td>T/I = 70/30</td>
<td>Tg = 162°C</td>
<td>Tm = 332°C</td>
</tr>
<tr>
<td>6000 Series</td>
<td>Pseudo Amorphous</td>
<td>T/I = 60/40</td>
<td>Tg = 160°C</td>
<td>Tm = 305°C</td>
</tr>
<tr>
<td>PEEK</td>
<td>Semi-crystalline</td>
<td></td>
<td>Tg = 143°C</td>
<td>Tm = 343°C</td>
</tr>
</tbody>
</table>
CONTROL OF CRYSTALLIZATION IS A KEY PARAMETER FOR A SUCCESSFUL SLS PROCESS

✦ PEKK offers an excellent compromise in properties
  ● Slow crystallization
  ● Moderate crystallinity (~20%)
  ● Excellent thermal stability combined with a moderate processing temperature (<300°C)
    → excellent powder recyclability

✦ But it has a complex melting behavior
  ● Two crystalline forms
  ● Strong influence of thermal history

Figure 9. Melting endotherms of PEKK(T/I) crystallized at various crystallization temperatures from the melt. All scans are at 10 °C/min.
CONTROL OF CRYSTALLIZATION IS A KEY PARAMETER FOR A SUCCESSFUL SLS PROCESS

Crystallization under isothermal conditions
- Melting above Tm and crystallization at T < Tm

![Graph showing fast and slow crystallization](image)

- Fast crystallization
- Slow crystallization
- Half Crystallization Time
CONTROL OF CRYSTALLIZATION IS A KEY PARAMETER FOR A SUCCESSFUL SLS PROCESS

» A complex melting behavior controlled by adequate thermal treatment
- Two crystalline forms before thermal treatment
- Only one after thermal treatment

![Graph showing melting behavior before and after thermal treatment]

- No thermal treatment
- Powder bed temperature
- Processing window
- After thermal treatment

Temperature (°C)
POWDER/PROCESS OPTIMIZATION

NON OPTIMIZED POWDER
- POWDER CAKING
- LOW INTERLAYER ADHESION
- NO POWDER RECYCLABILITY

OPTIMIZED POWDER
- NO POWDER CAKING
- GOOD INTERLAYER ADHESION
- POWDER RECYCLABILITY
MECHANICAL PROPERTIES

♦ SLS vs Injection Molding (IM)
  ● Comparison between SLS & IM is not straightforward
♦ SLS and IM grades are not necessary identical (differences in molecular weight, stabilization, formulation)
♦ Difference in crystallization
  ● Absence of pressure when processing in SLS → porosity

<table>
<thead>
<tr>
<th></th>
<th>IM*</th>
<th>SLS (xy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.27</td>
<td>1.30</td>
</tr>
<tr>
<td>Stress @ yield</td>
<td>(88MPa)</td>
<td>95Mpa**</td>
</tr>
<tr>
<td>Strain @ break</td>
<td>(&gt;60%)</td>
<td>2-4%</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>(2.9GPa)</td>
<td>4.0Gpa**</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>(3GPa)</td>
<td>4.2Gpa**</td>
</tr>
</tbody>
</table>

* Mostly amorphous due to fast cooling
** Values for z-direction are significantly lower
PARTICLE SIZE AND SURFACE SMOOTHNESS

EXAMPLE OF PA12 RILSAMID®

Average particle size = 42 µm

Average particle size = 56 µm

SMOOTH SURFACE

ROUGH SURFACE
AERO AND AUTO APPLICATIONS

AIR DUCTS FOR AIRPLANES
(PA11 AND PEKK)

BRAKE FLUID TANK IN AUTOMOTIVE
In SLS of plastics the challenge is the powder recycling

- Typical figures are:
  - 20% of powder present in the bed is used for the part construction
  - 50% recycled
  - 30% waste

- The new design saves on average 10 to 25% raw material

- Positive balance if the waste is < 10%

Aircraft fitting before and after structural shape optimization

Source: Oxford Performance Materials
CONCLUSIONS

1. Fast growing market for polymers

2. Freedom in design which allows
   - Weight reduction
   - Material savings

3. Cost effective for small series

4. For SLS absolut need to adjust powder properties