WORLD MATERIALS FORUM

POLYMERS IN ADDITIVE MANUFACTURING

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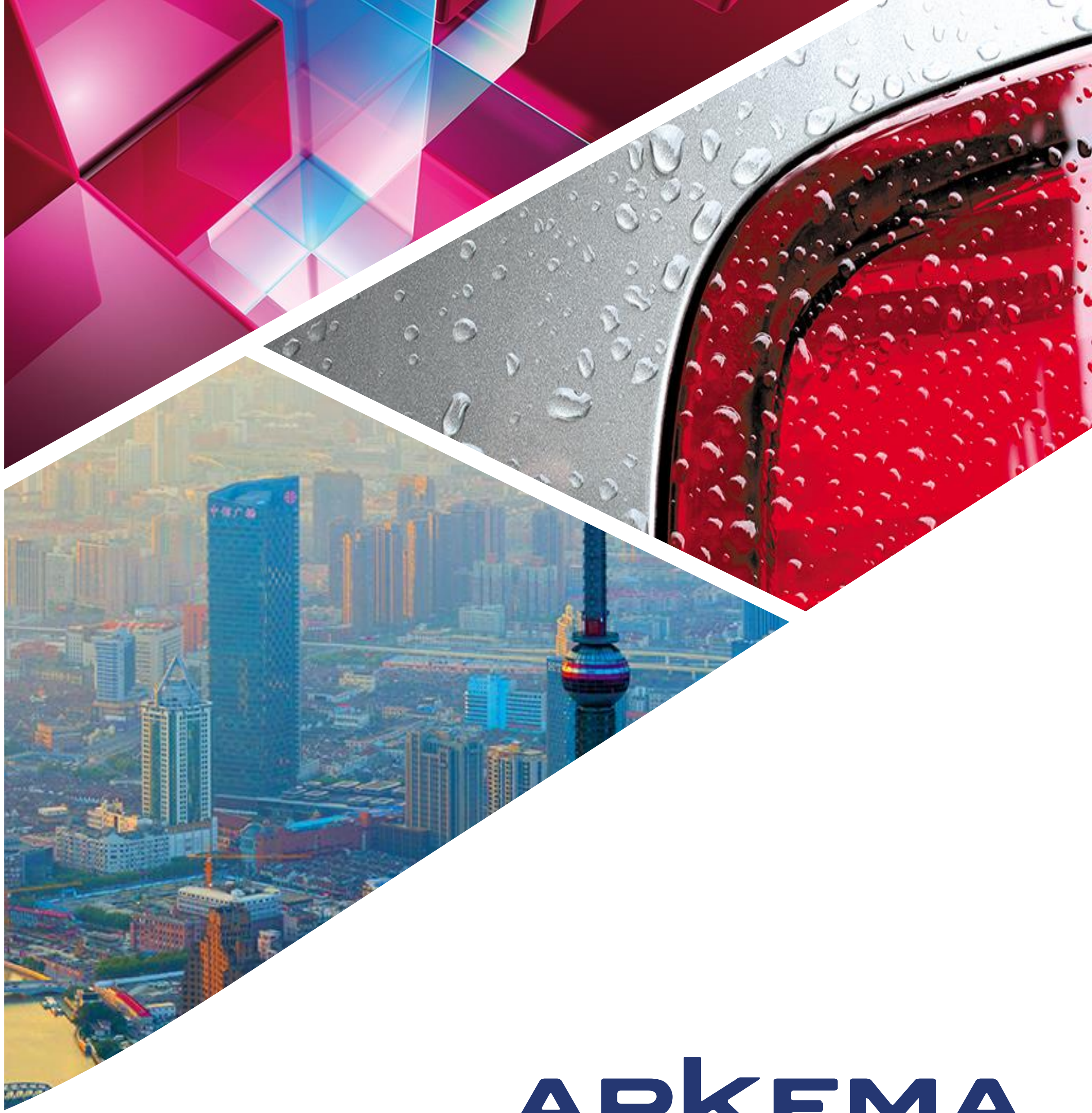
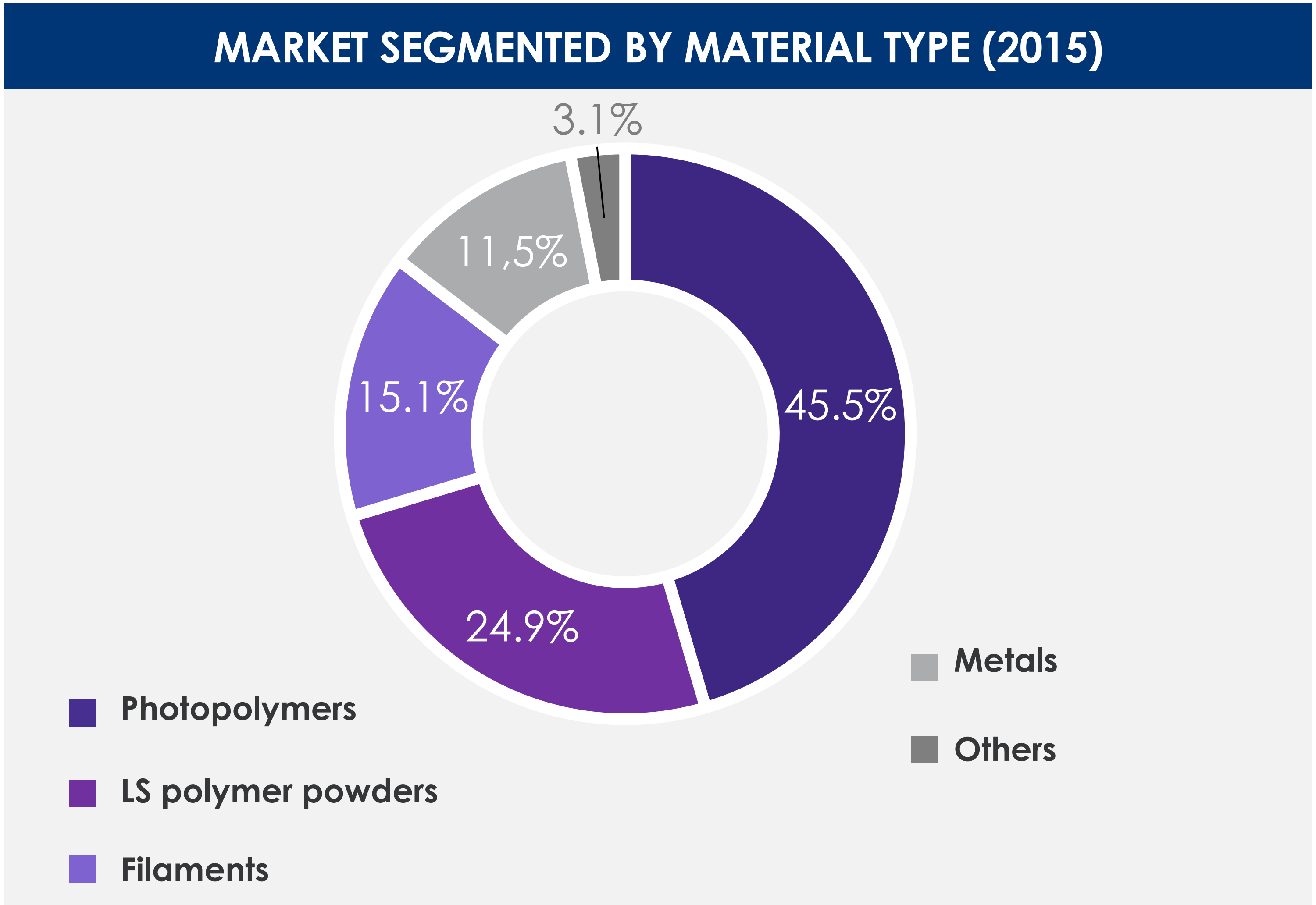
9 & 10 June 2016



ARKEMA
INNOVATIVE CHEMISTRY

MATERIALS IN ADDITIVE MANUFACTURING

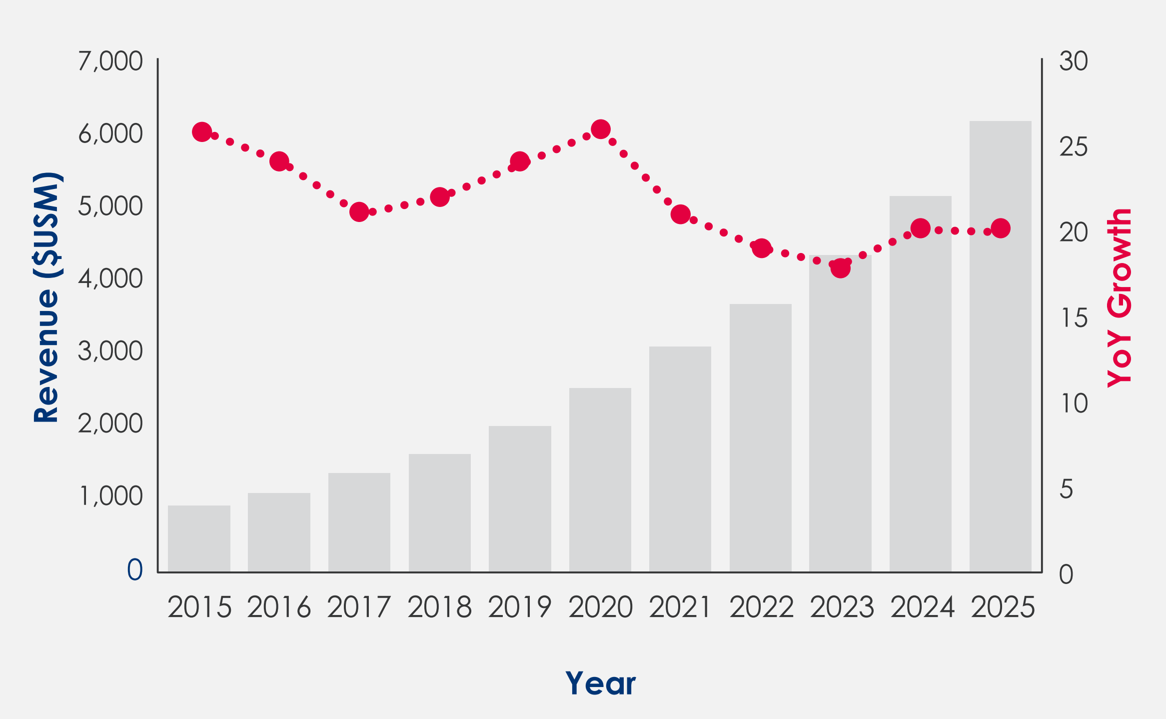


Source: Wohlers Associates, Inc

MARKET FOR POLYMER MATERIALS

Fast growing market for polymer materials

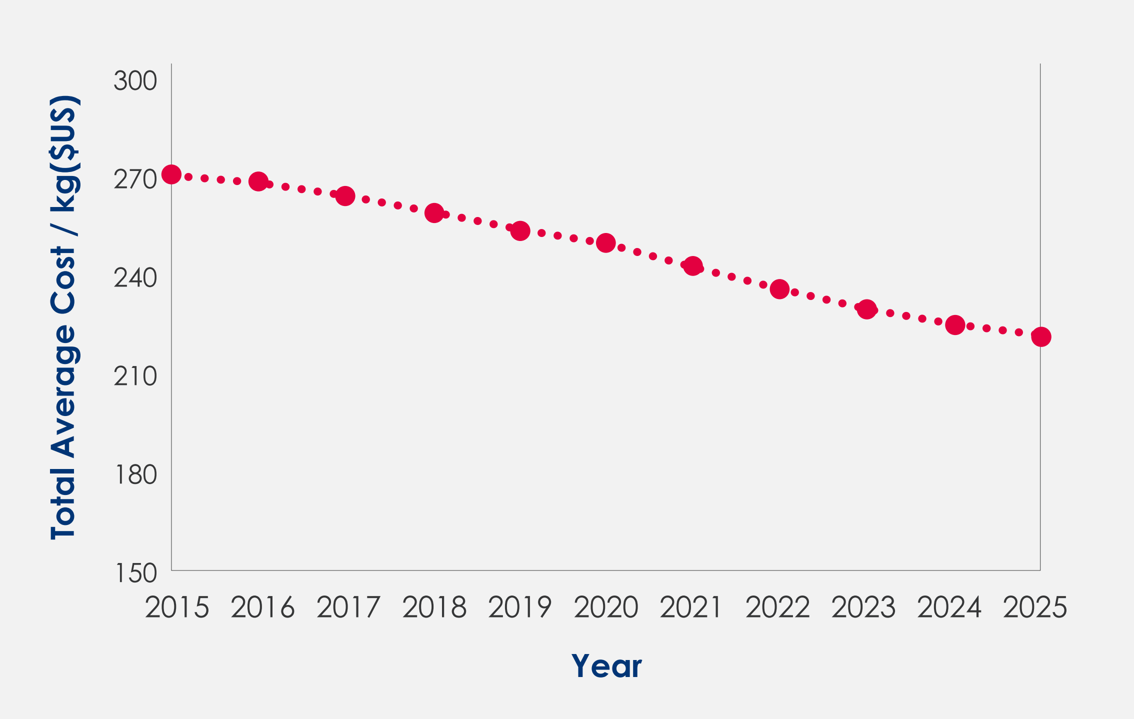
- $150M in 2005, $850M in 2015, $6,200m in 2025
- Annual growth ~25%



Source: SmartechMarkets 2015

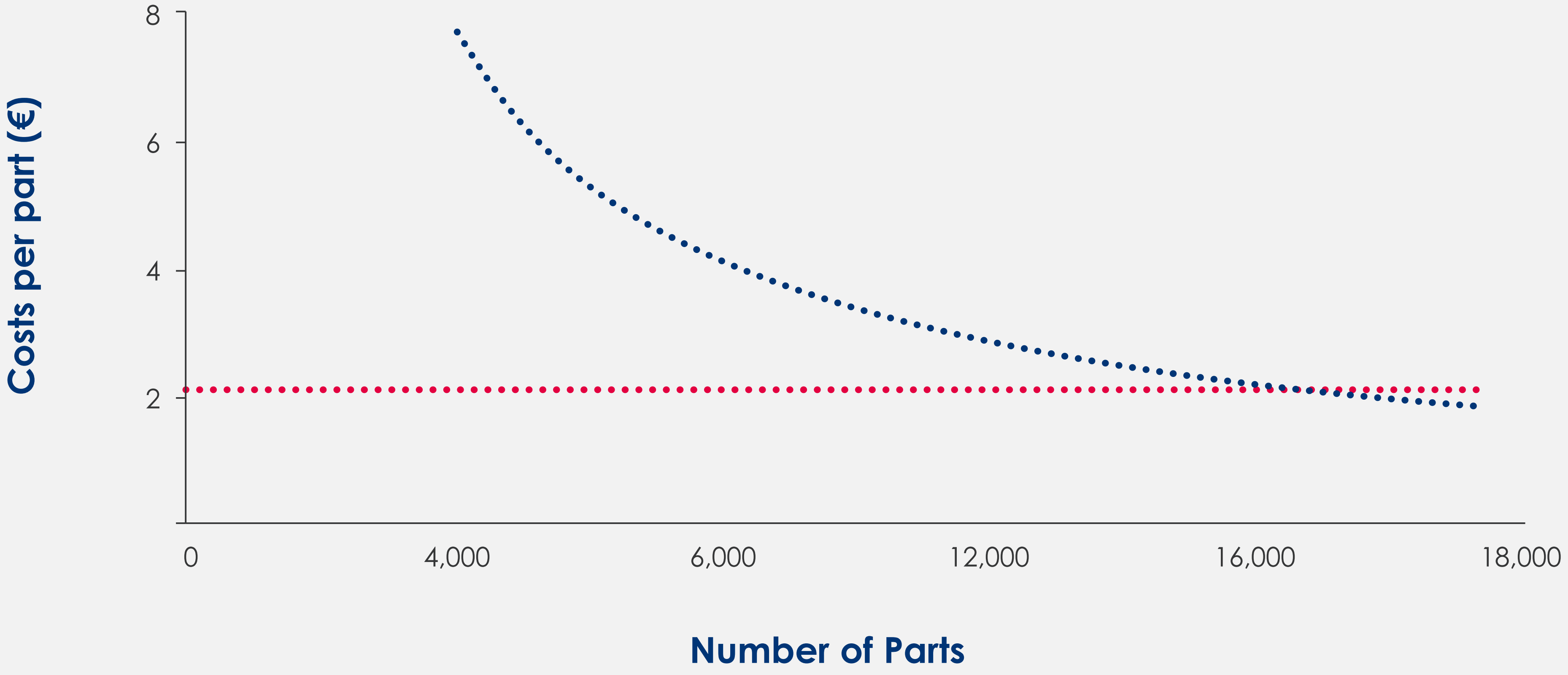
Slow decrease of the average cost of polymer materials

- From $270/kg in 2014 to $220/kg in 2025



INDUSTRIAL PRODUCTION

COST EFFECTIVE FOR SMALL SERIES



Additive Manufacturing

Injection Molding

MAIN POLYMER FAMILIES

- **Automotive**
  - (ABS, PA)
- **Aeronautic**
  - (PA, PEI, PEKK, PEEK)
- **Sport**
  - (PA, TPU, Photopolymers)
- **Consumer products**
  - (ABS, PLA, Photopolymers)
- **Electronic**
  - (Photopolymers)
- …

Aircraft fitting before and after structural shape optimization

Source: Oxford Performance Materials

Air duct for laminar flow

Source: EOS

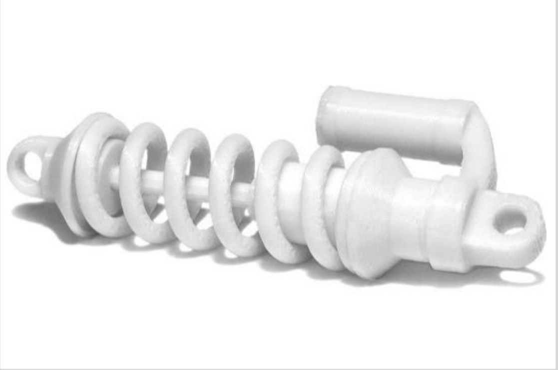
MARKETS AND APPLICATIONS FOR POLYMER 3D PRINTING

INDUSTRY	CURRENT APPLICATIONS	FUTURE TARGET APPLICATIONS	3D PRINTING TECHNOLOGIES
AEROSPACE	Non critical cabin and structural components, assembly tooling	Structural components, high volume cabin components	SLS, material extrusion
AUTOMOTIVE	Prototypes, assembly tooling, functional test parts for concept cars	Interior components, customized parts for product differentiation	SLS, material extrusion, SLA, material jetting
CONSUMER PRODUCTS	Models, prototypes, custom low complexity products	On-demand consumer products and end use components	SLA, material jetting, binder jetting,
MEDICAL	Anatomical models, surgical tools and guides, implants, upper extremity prosthetics	High realism and multi material models, load bearing implants, lower extremity prosthetics	SLA, SLS, Material jetting

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**

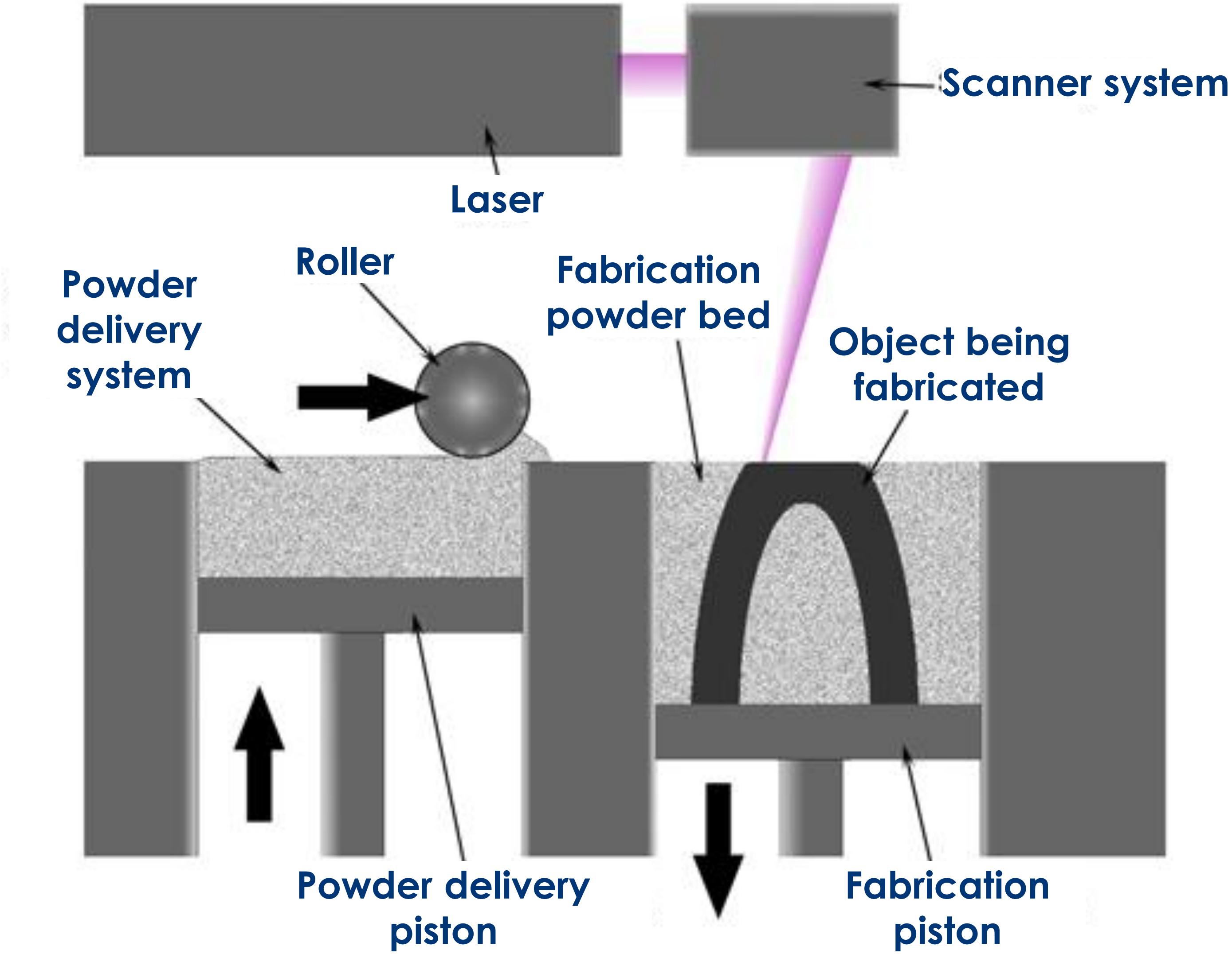
VAT PHOTOPOLYMERIZATION
(Stereolithography, SLA)

- **Photocured polymers**
- **Good surface finishing**

MATERIAL JETTING
(PolyJet, MultiJet)

- **Photocured polymers**
- **Multimaterial, multicolor**

LASER SINTERING WITH HIGH TEMPERATURE POLYMERS

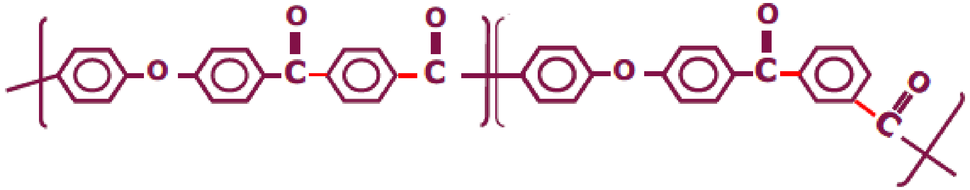


Source: Wikipedia

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

Terephaloyle  Isophtaloyle

GRADES KEPSTAN		T/I RATION	TG	TM
8000 Series	**Semi-crystalline**	**T/I = 80/20**	**Tg = 165°C**	**Tm = 358°C**
7000 Series	**Semi-crystalline**	**T/I = 70/30**	**Tg = 162°C**	**Tm = 332°C**
6000 Series	**Pseudo Amorphous**	**T/I = 60/40**	**Tg = 160°C**	**Tm = 305°C**
PEEK	Semi-crystalline		Tg = 143°C	Tm = 343°C

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

Gardner, *Polymer* 1992

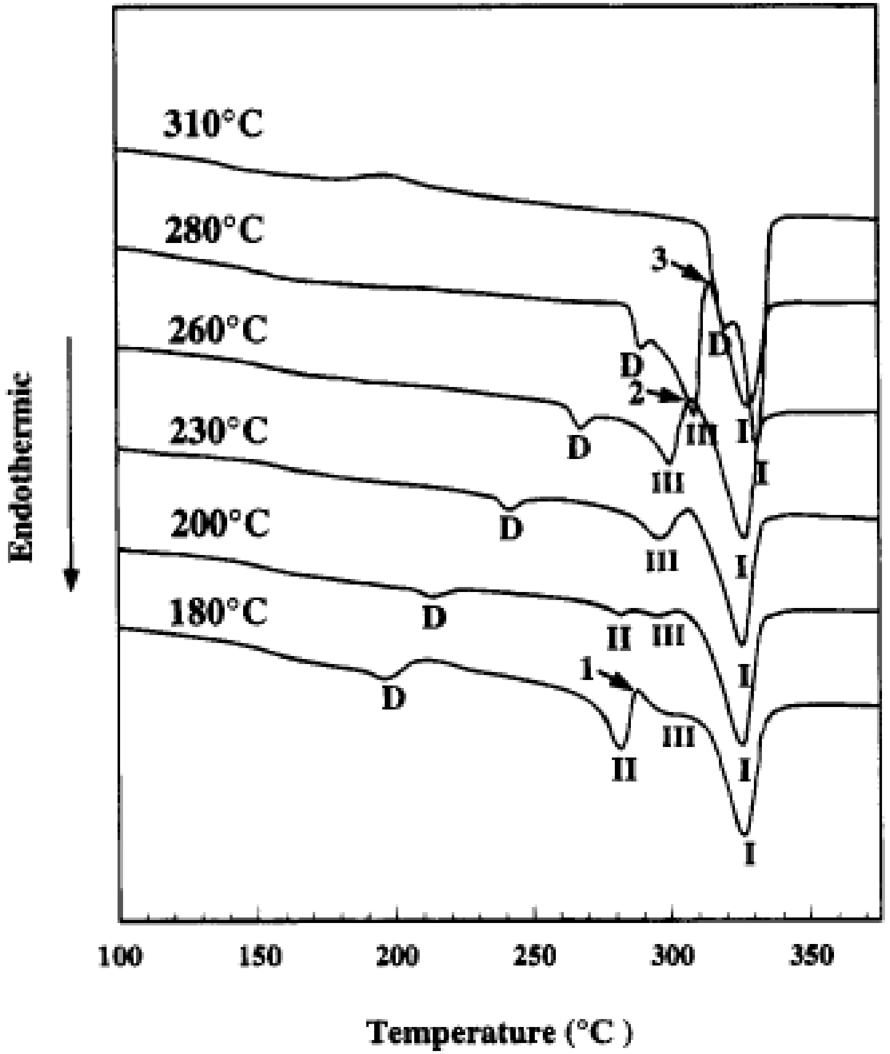
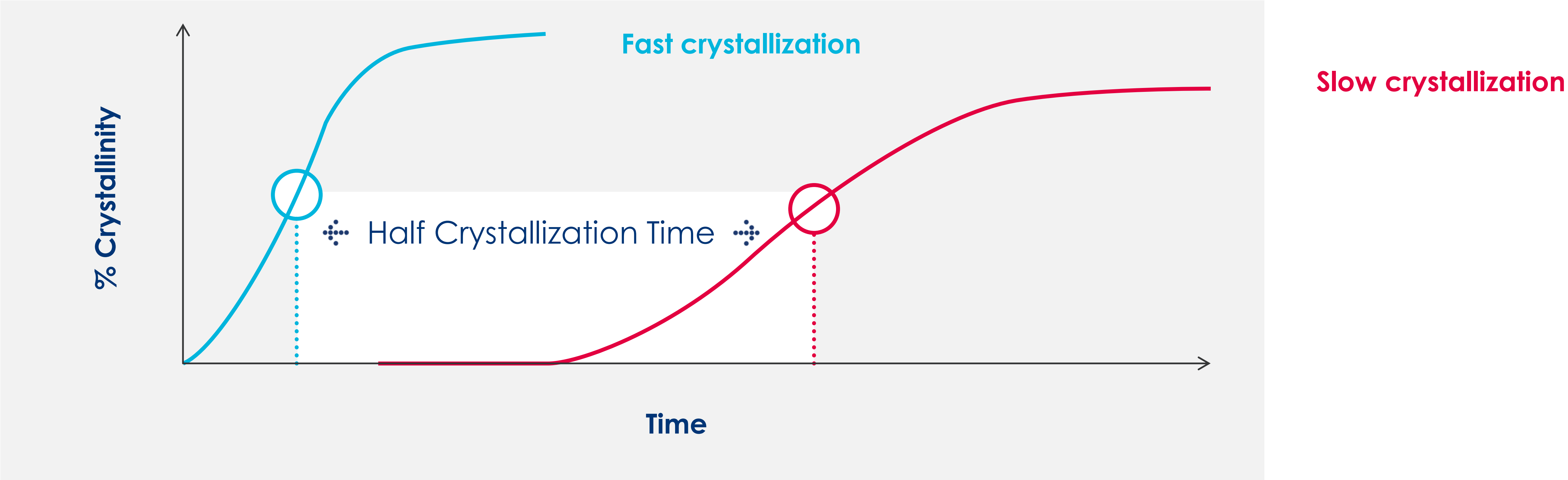


Figure 9. Melting endotherms of PEKK(T/I) crystallized at various crystallization temperatures from the melt. All scans are at 10 °C/min.

CONTROL OF CRYSTALLIZATION IS A KEY PARAMETER FOR A SUCCESSFUL SLS PROCESS

Crystallization under isothermal conditions

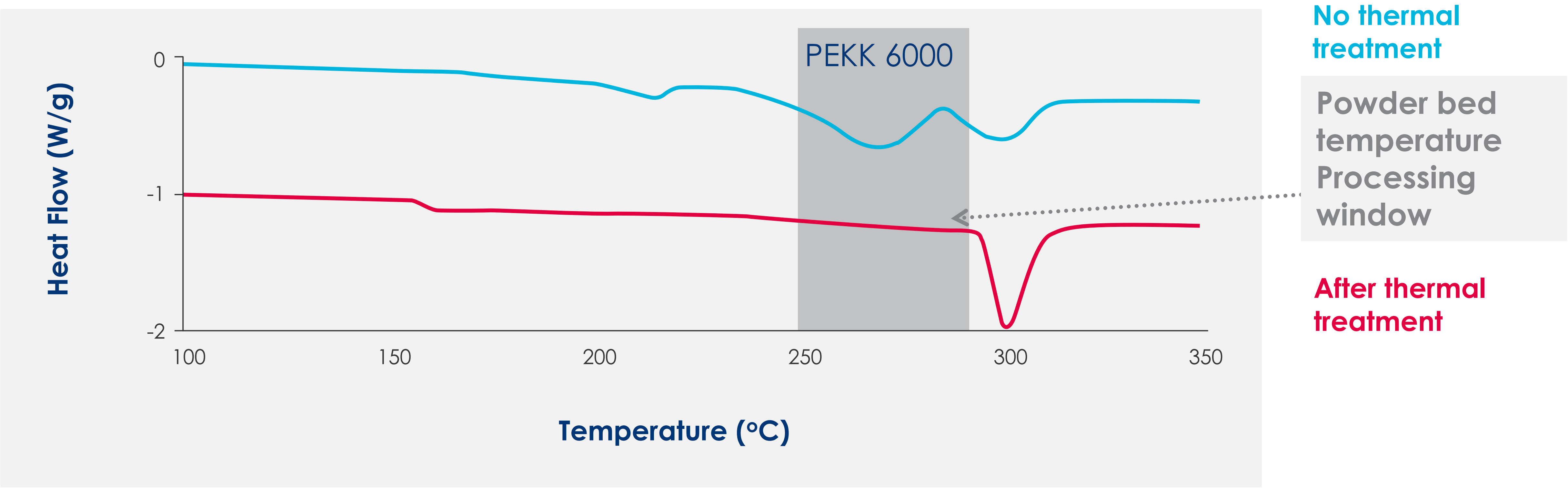
- Melting above Tm and crystallization at T < Tm



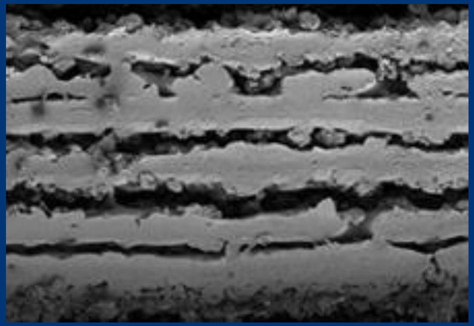
CONTROL OF CRYSTALLIZATION IS A KEY PARAMETER FOR A SUCCESSFUL SLS PROCESS

A complex melting behavior controlled by adequate thermal treatment

- Two crystalline forms before thermal treatment
- Only one after thermal treatment

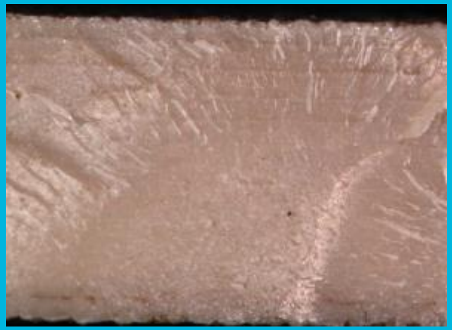


POWDER/PROCESS OPTIMIZATION



NON OPTIMIZED POWDER

- POWDER CAKING
- LOW INTERLAYER ADHESION
- NO POWDER RECYCLABILITY



OPTIMIZED POWDER

- NO POWDER CAKING
- GOOD INTERLAYER ADHESION
- POWDER RECYCLABILITY

MECHANICAL PROPERTIES

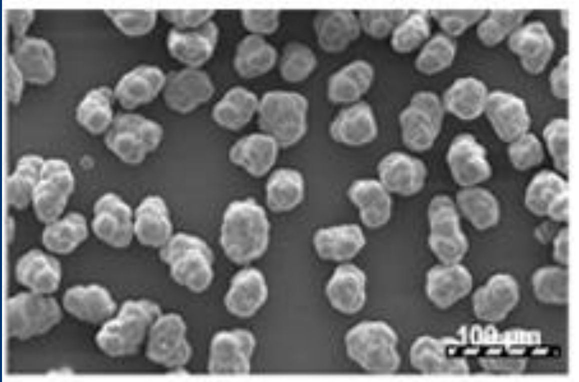
- **SLS vs Injection Molding (IM)**
  - **Comparison between SLS & IM is not straightforward**
- **SLS and IM grades are not necessary identical (differences in molecular weight, stabilization, formulation)**
- **Difference in crystallization**
  - **Absence of pressure when processing in SLS → porosity**

	PEKK 6000	
	IM*	**SLS (xy)**
Density	1.27	1.30
Stress @ yield	(88MPa)	95Mpa**
Strain @ break	(>60%)	2-4%
Tensile modulus	(2.9GPa)	4.0Gpa**
Flexural modulus	(3GPa)	4.2Gpa**

* Mostly amorphous due to fast cooling
** Values for z-direction are significantly lower

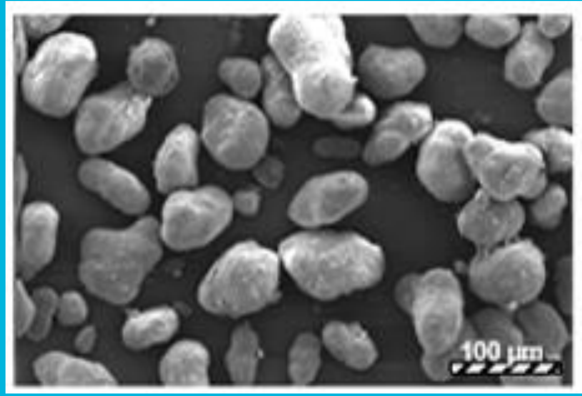
PARTICLE SIZE AND SURFACE SMOOTHNESS ⁘ EXAMPLE OF PA12 RILSAMID®

Average particle size = 42 µm

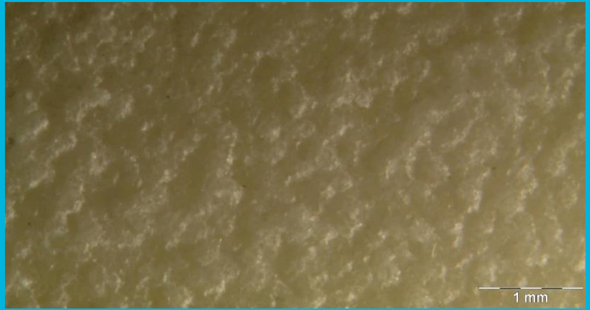


SMOOTH SURFACE

Average particle size = 56 µm



ROUGH SURFACE



AERO AND AUTO APPLICATIONS

AIR DUCTS FOR AIRPLANES (PA11 AND PEKK)

BRAKE FLUID TANK IN AUTOMOTIVE

MATERIALS-PROCESS EFFICIENCY

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**

Aircraft fitting before and after structural shape optimization

Source: Oxford Performance Materials

- **Positive balance if the waste is < 10%**

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