

"Fusion based additive processing of biopolymers"

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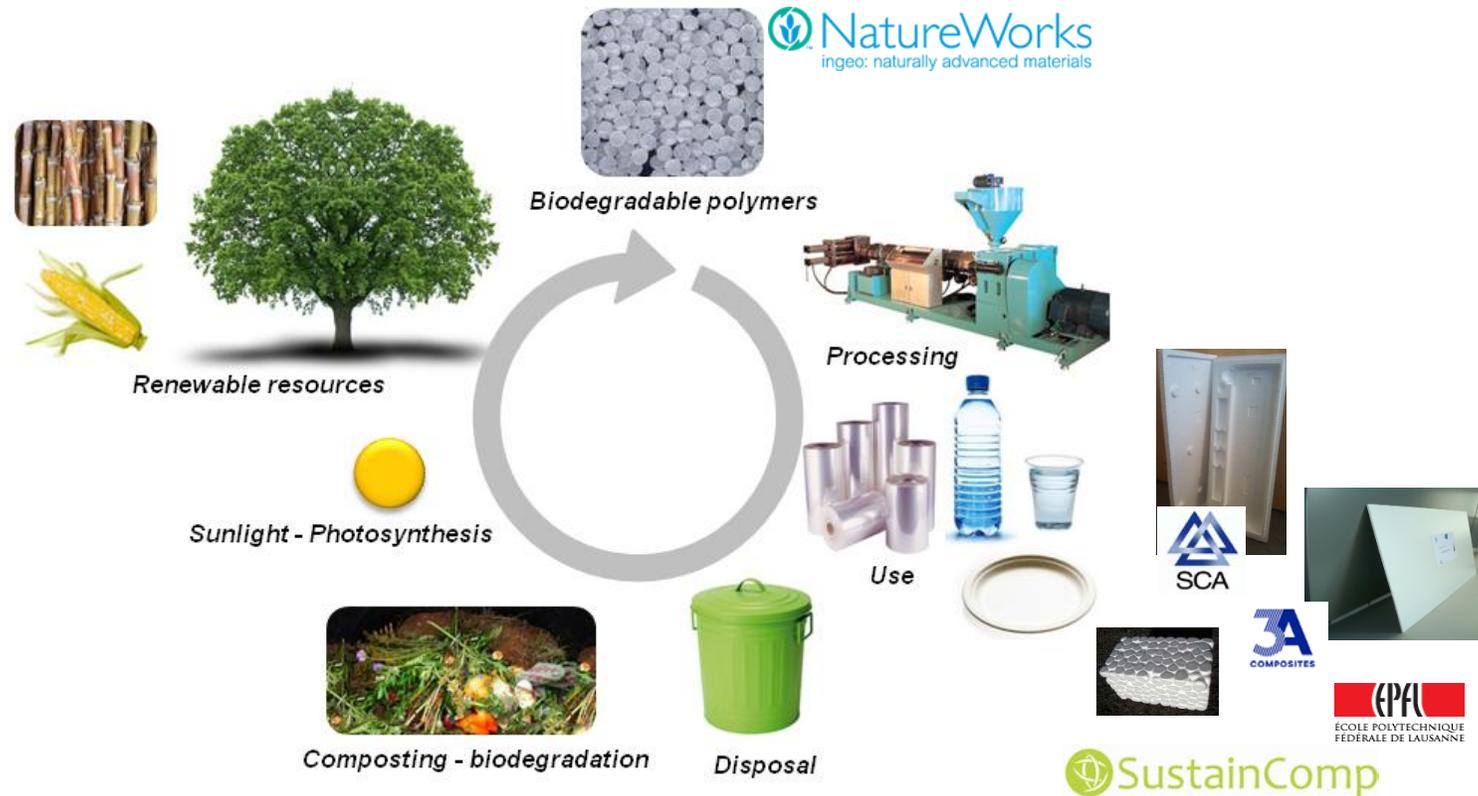
ltc.epfl.ch

AMIG 3.12.14

- **Biopolymers**
 - Renewable polymers
 - Biomedical grade polymers
- **Processing**
 - Fusion of thermoplastic polymers
 - Materials transformation phenomena
 - Processing biopolymer composites
- **Additive manufacturing**
- **Current R&D**
- **Applications**

Biopolymers

- Renewable polymers
 - From petroleum and from waste vegetables
 - The ' Polylactide (PLA) ' family



Biomed polymers

- **Biocompatible polymers**



Composite ortho and prosthesis



ICRC Limb prosthesis



Stryker Primary Knee Replacement System



Medtronic Talent Abdominal Stent Graft



RootReplica® (Sunstar DS AG)

- **Bioresorbable polymers**

Biomed polymers

**Custom-made
complex shapes**

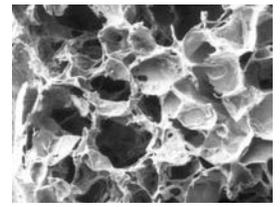
Sutures



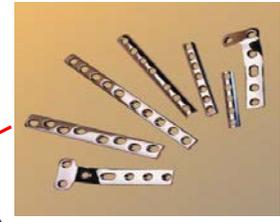
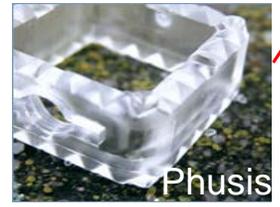
Dental membranes



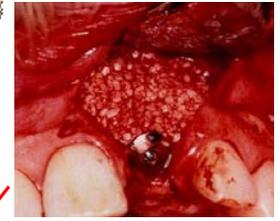
Matrices for tissue engineering



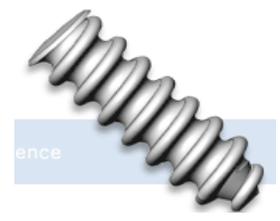
Vertebral cages



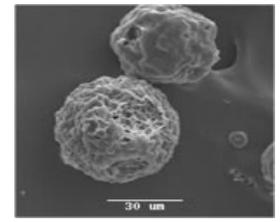
Fixation elements for maxillofacial surgery



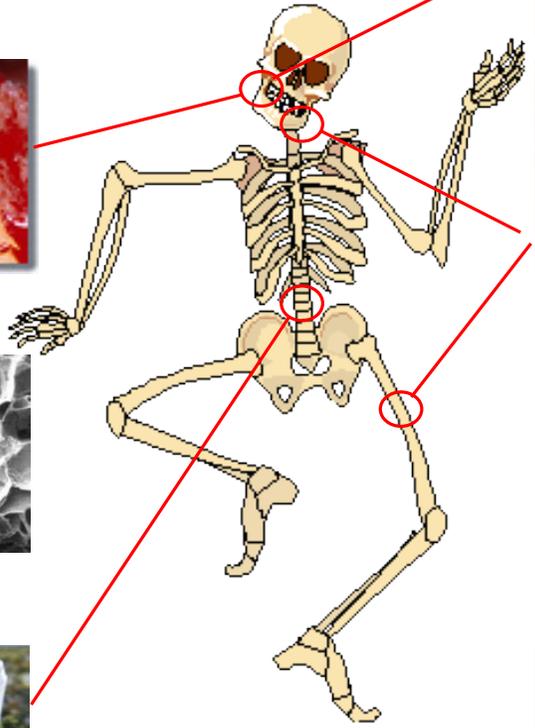
Biomaterials for bone augmentation



Bioresorbable screws (fixation)



Drug release

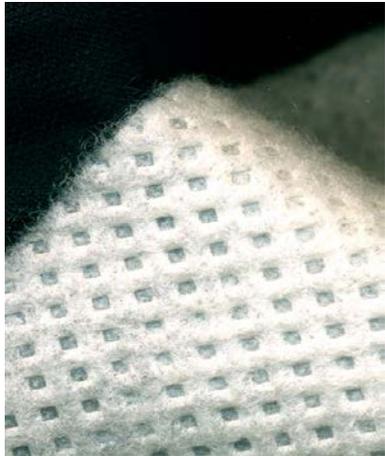


It's about scale

- **Material structure at different scales**
- **Processing steps to control the structure and properties**
- **Scaling up to product**

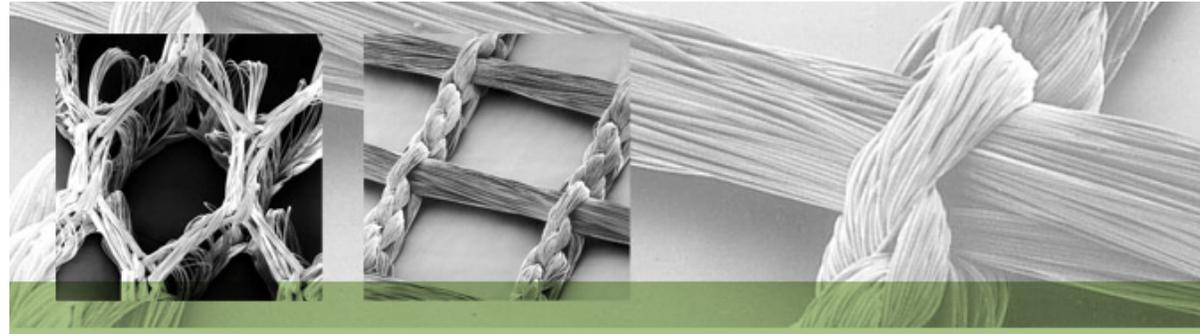
Macro-meso-micro

- Textiles



<http://www.bmsri.com>

cm



Sofradim Covidien.com

mm

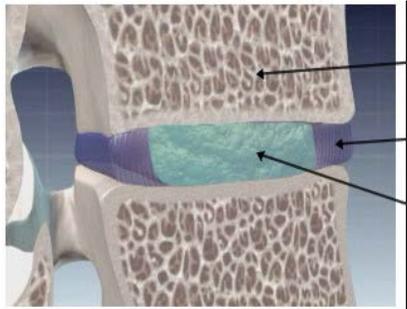
μm

- Yarns of fibres are placed and oriented to optimize local stiffness
- Non-wovens, wovens, knitted, embroidered textiles
- Angiogenesis, vascularization

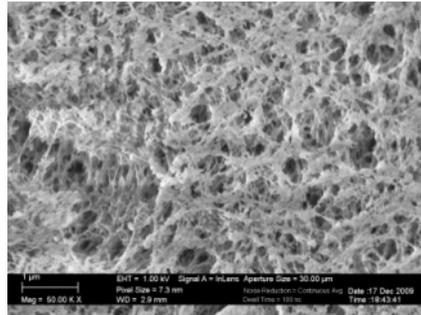
Macro-meso-micro-nano

Hydrogel

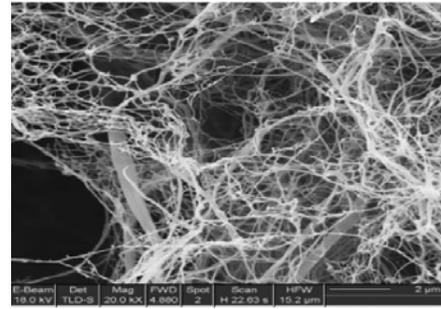
• Hydrogel Biocomposites



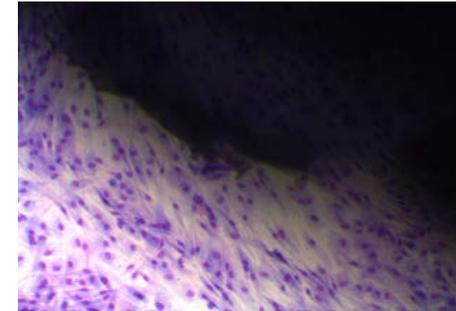
cm



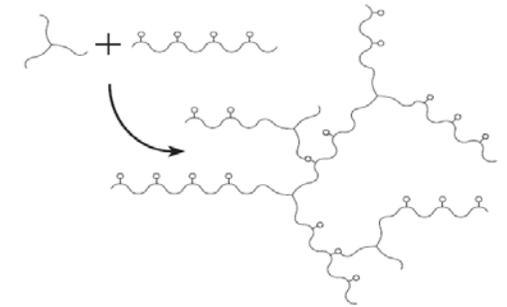
mm



μm



nm

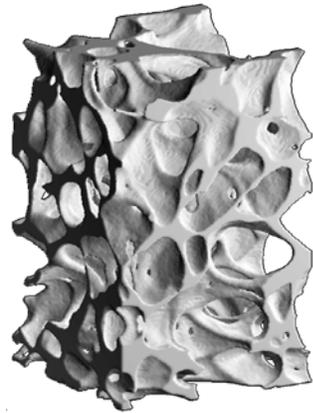


- Soft porous polymers containing liquids
- Photo-hydrogels reinforced by a network of cellulose microfibrils
- Stiffness, swelling... tailored by the level of molecules crosslinking

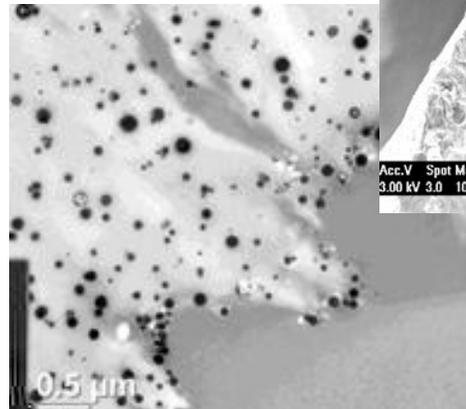
• Polymer Cellular Biocomposites



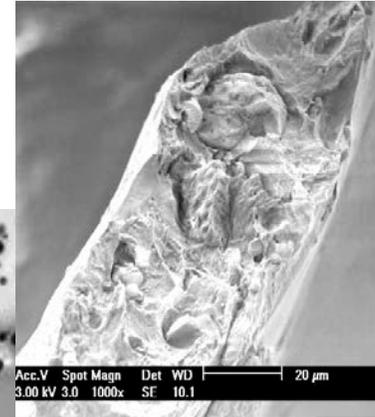
cm



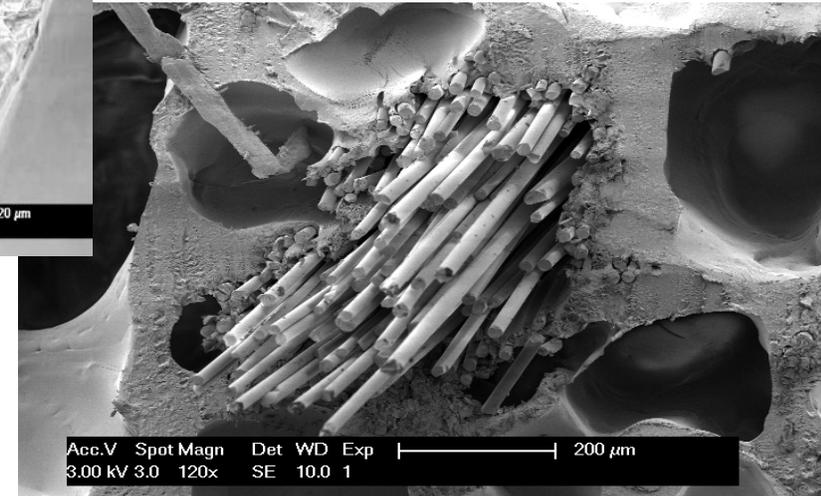
mm



0.5 μm



Acc.V Spot Magn Det WD
3.00 kV 3.0 1000x SF 10.1

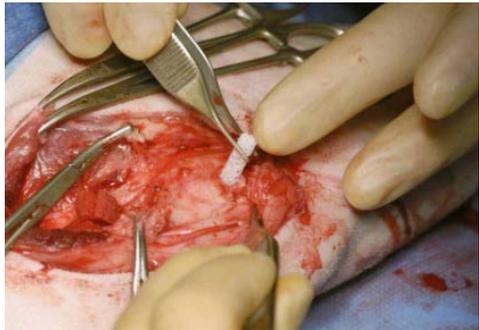


Acc.V Spot Magn Det WD Exp
3.00 kV 3.0 120x SE 10.0 1

μm

- Particles are processed into polymers for stiffness and osteoconductivity
- Yarns of fibres provide anisotropic composite foams
- Bone regeneration

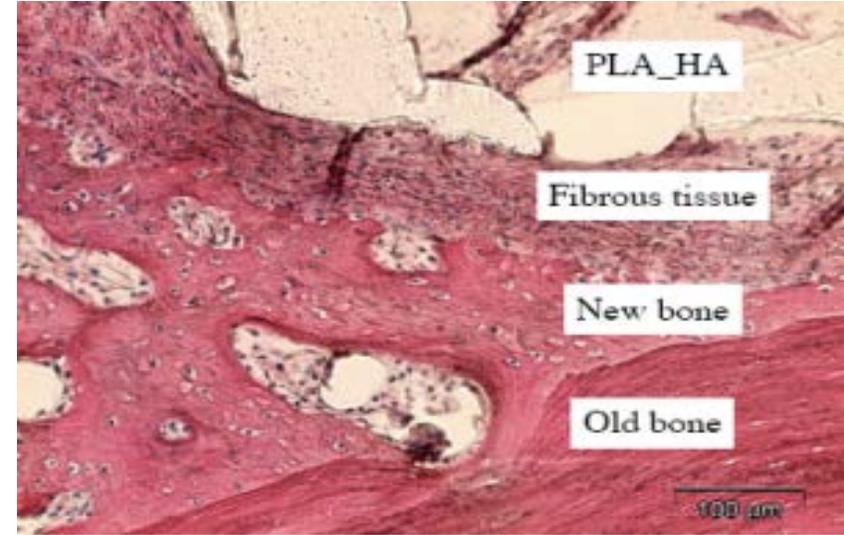
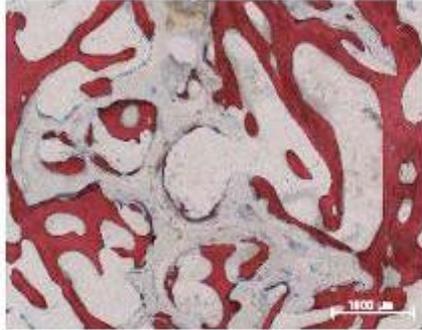
- Interfaces: Material-Living tissues



cm



mm



μm

- **Biopolymers**
 - Renewable polymers
 - Biomedical grade polymers
- **Processing**
 - Fusion of thermoplastic polymers
 - Materials transformation phenomena
 - Processing biopolymer composites
- **Additive manufacturing**
- **Current R&D**
- **Applications**

Processes

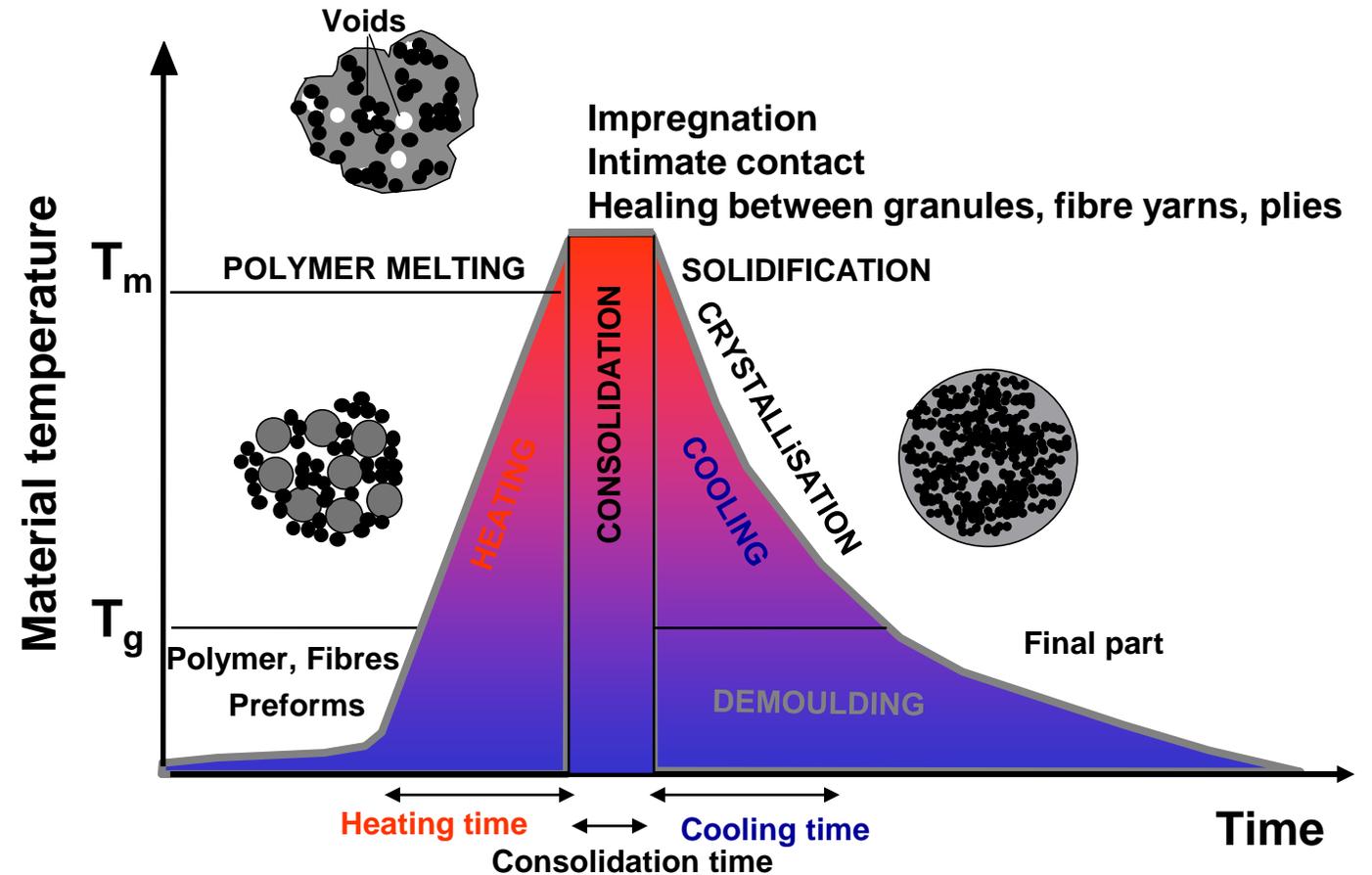
- **Nozzle based processes**
 - **Molten polymer**
 - Extrusion
 - Fused Deposition Modelling, FDM
 - Filament Deposition
 - **Liquids, binders**
 - 3D printing
- **Light-based processes**
 - **Stereolithography, SLA**
 - Mask-based or direct writing methods
 - **Selective laser sintering SLS**

Materials

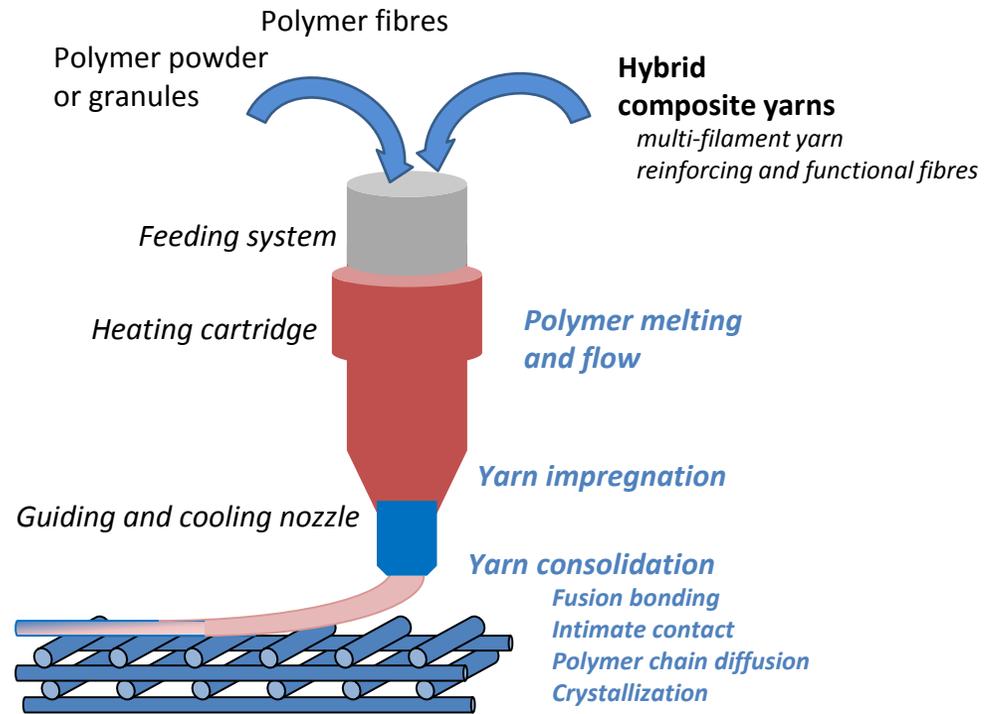
- **Thermoplastic polymers**
 - ABS
 - PC
 - PA
 - PEEK
 - Polycaprolactones PCL
 - Polylactides PLA, PGA,
 - Copolymers, blends
 - PEOT/PBT
- **Photo-polymers**
 - Hydrogels, PEG, PEG-MA, PLA-PEG
 - Modified PCL, polytrimethylcarbonate...
 - Limited choice of photo-polymerizable biomaterials
- **Conductive polymers**
 - Polyacetylene
 - Polypyrrole
 - Polythiaphene
 - Polyaniline

Processing thermoplastic polymers

- Material transformation phenomena and window
- Processes and processing windows

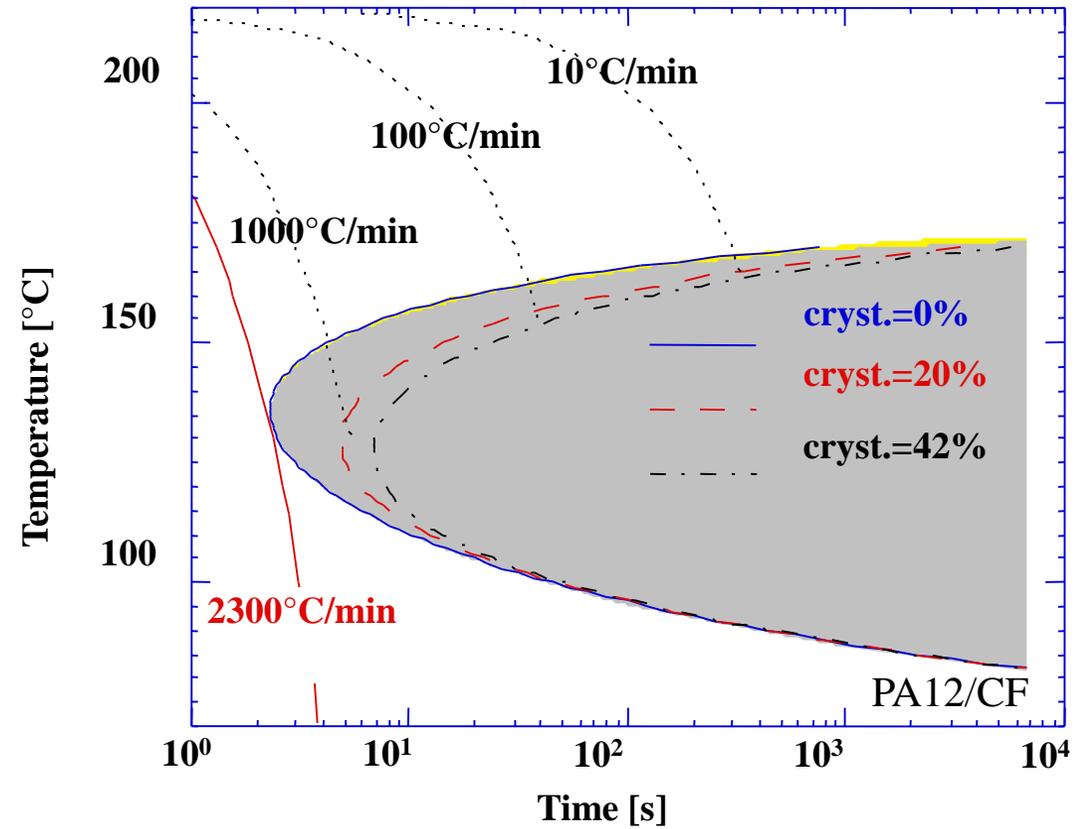


Fused Deposition Modelling

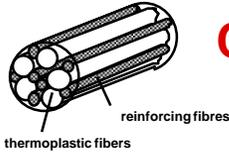


Consolidation : crystallization

PA12



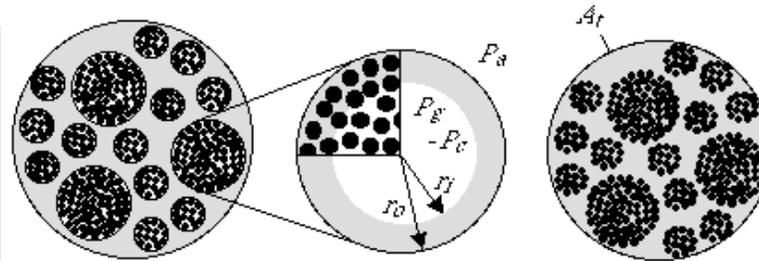
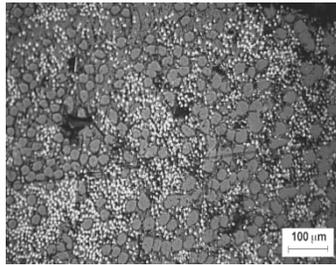
Consolidation : porosity content



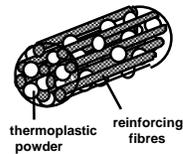
COMMINGLED YARN (CY)

$$\Delta t = \frac{\eta(1-V_f)}{K(P_a + P_c - P_v(r_i))} \left[\frac{r_i^2}{2} \ln\left(\frac{r_i}{r_o}\right) - \frac{R_i^2}{2} \ln\left(\frac{R_i}{r_o}\right) - \frac{r_i^2}{4} + \frac{R_i^2}{4} \right]$$

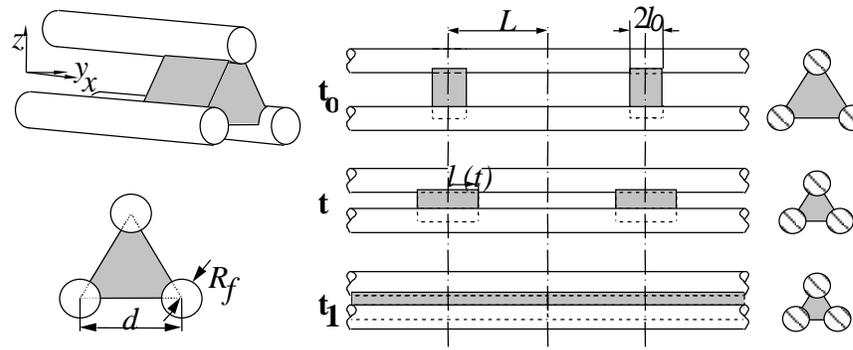
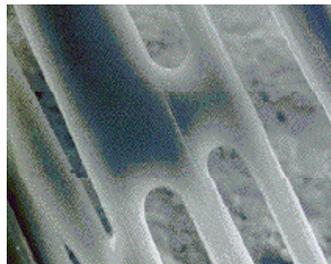
$$X_v = \frac{\sum_{k=1}^n \pi N_b^k r_k^2 (1-V_f)}{A_t + \sum_{k=1}^n \pi N_b^k r_k^2 (1-V_f)}$$



Onset of Yarn Consolidation → Fiber Bundle Impregnation → Full Yarn Consolidation



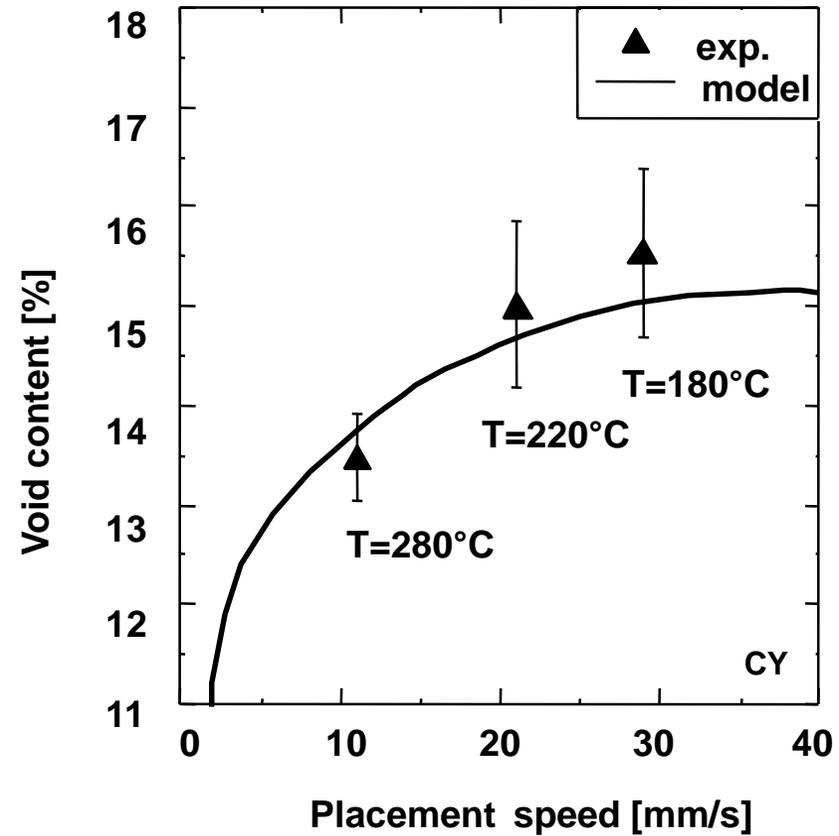
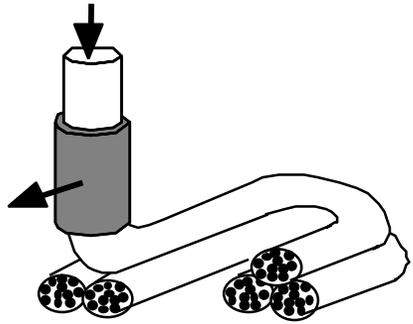
POWDER IMPREGNATED TOW (PIT)



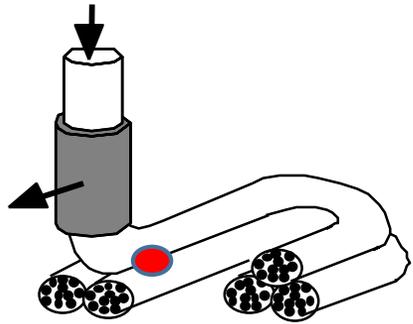
$$t_{impregnation} = \frac{128}{135} \frac{\eta}{P_a} \left(\frac{V_{fl}}{V_{ml}} \right)^4 \left(\frac{R_m}{R_f} \right)^6 \left[\left(\frac{l}{L} \right)^5 - \left(\frac{l_0}{L} \right)^5 \right]$$

$$X_v = \frac{1 - \left(\frac{l}{L} \right)}{1 + \left(\frac{l}{L} \right) \left(\frac{V_{fl}}{V_{ml}} \right)}$$

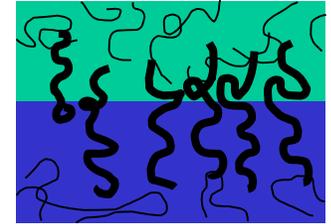
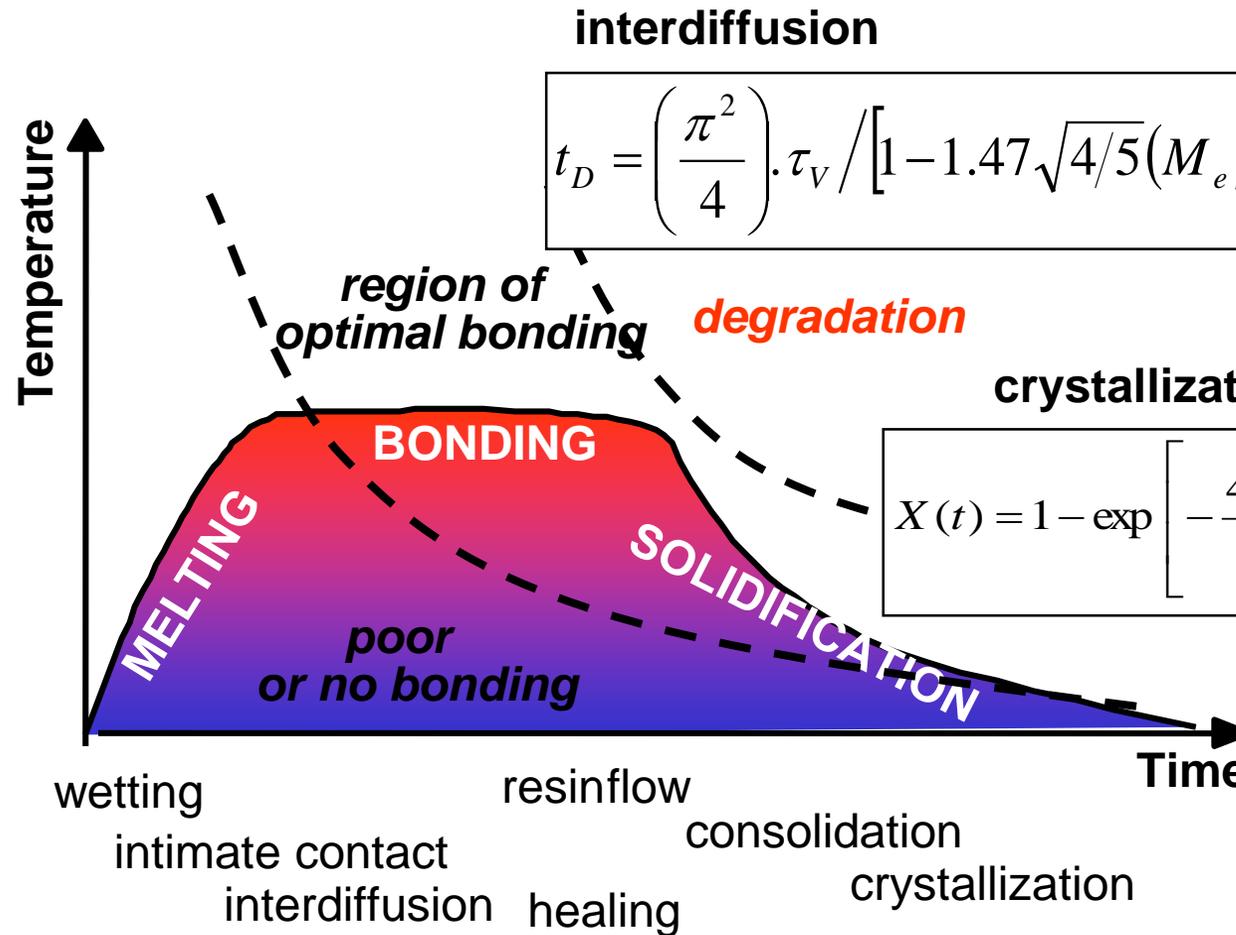
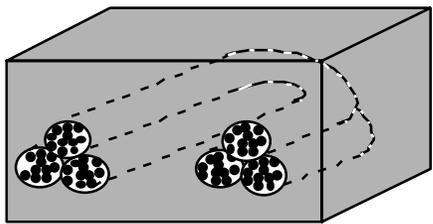
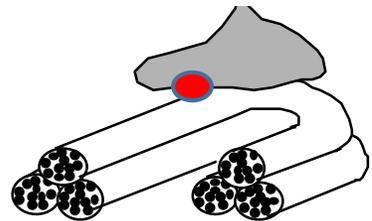
An example: Yarn placement



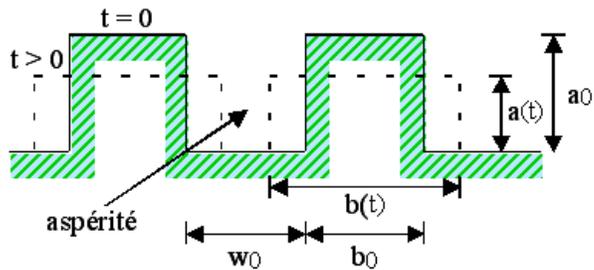
Fusion bonding



Polymer injection



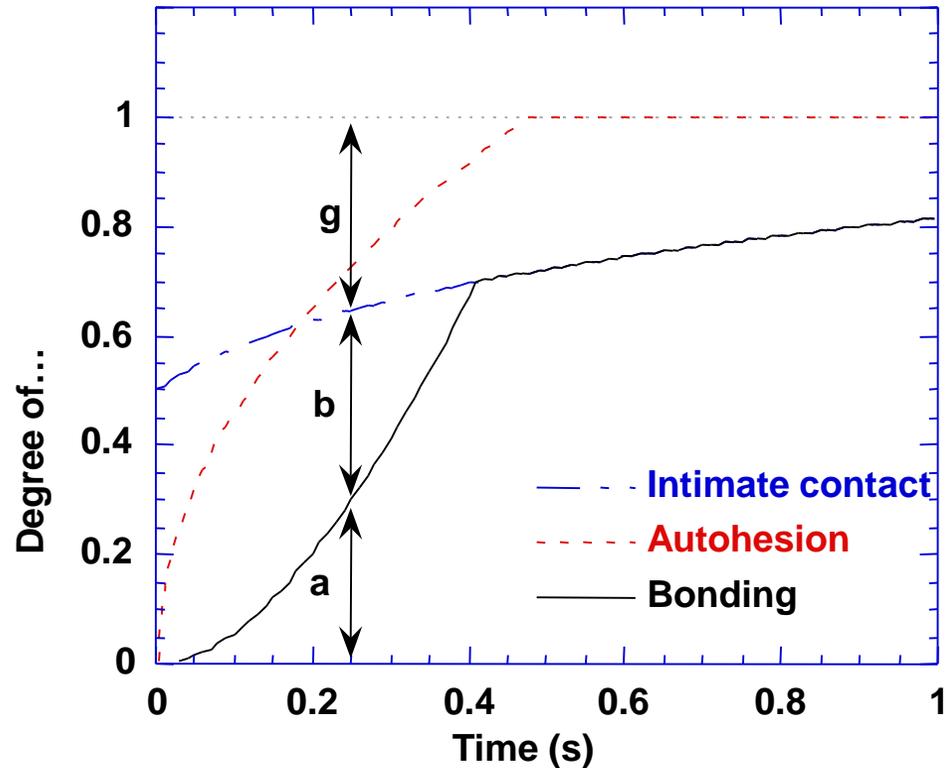
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intimate contact

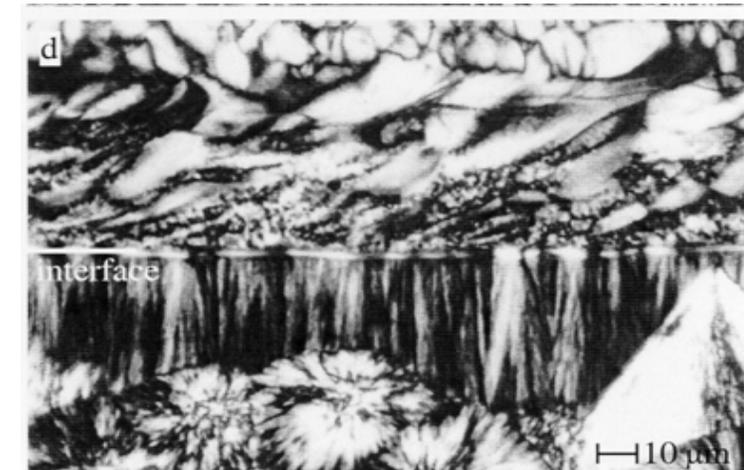
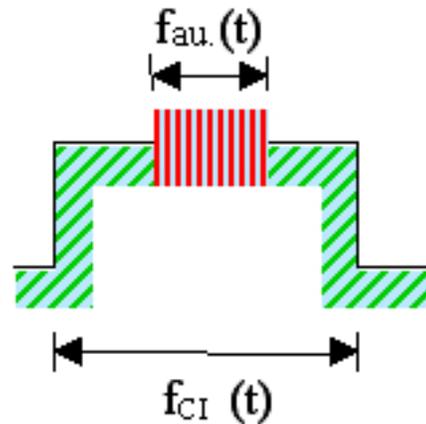
$$t_{CI}(T) = \frac{\eta(T)}{5P} \left(\frac{f_0 + \omega_0}{f_0} \right)^{-1} \left(\frac{a_0}{f_0} \right)^{-2} \left[\left(\frac{f_0 + \omega_0}{f_0} \right)^5 - 1 \right]$$

Fusion bonding : kinetics



Degree of progression for intimate contact, autohesion and thus bonding for polyamide 12 at 180°C under 2 MPa of contact pressure.

$$D_s(\tau) = \sum_{i=1}^{\tau_{c.i.}/dt} \left[\Delta D_{c.i.}(\tau_i - \tau_{i-1}) \cdot \sum_{j=i+1}^{\tau_{au.}/dt} D_{au.}(\tau_j, T_j) \right]$$



**Non isothermal
interfacial crystallization in PP**

Processing biomed polymers

- **Additional phenomena**

- **Degradation during processing**

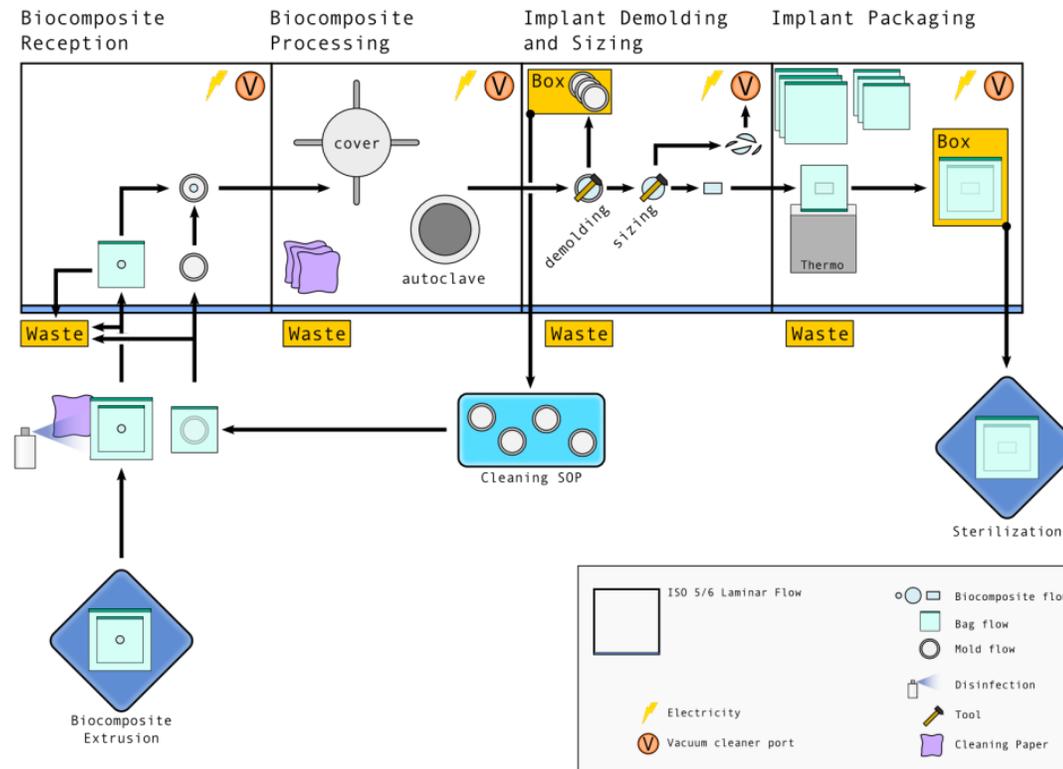
- Drying
- Molecular weight drop

- **Contamination**

- Environment
- Tools

- **Sterilization**

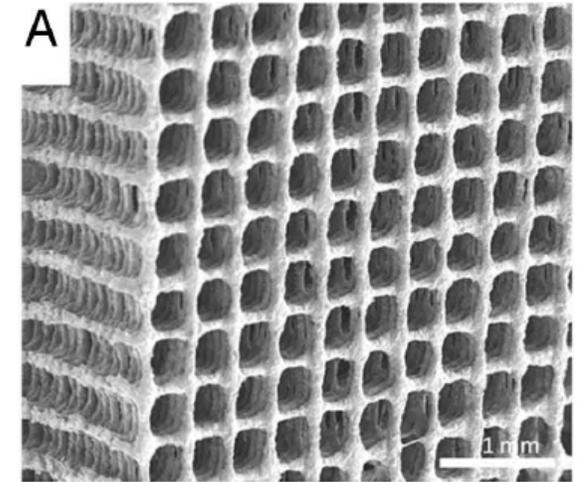
- EtOH
- Gamma



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- **Additive manufacturing**
- **Current R&D**
- **Applications**

Additive manufacturing : polymer solutions

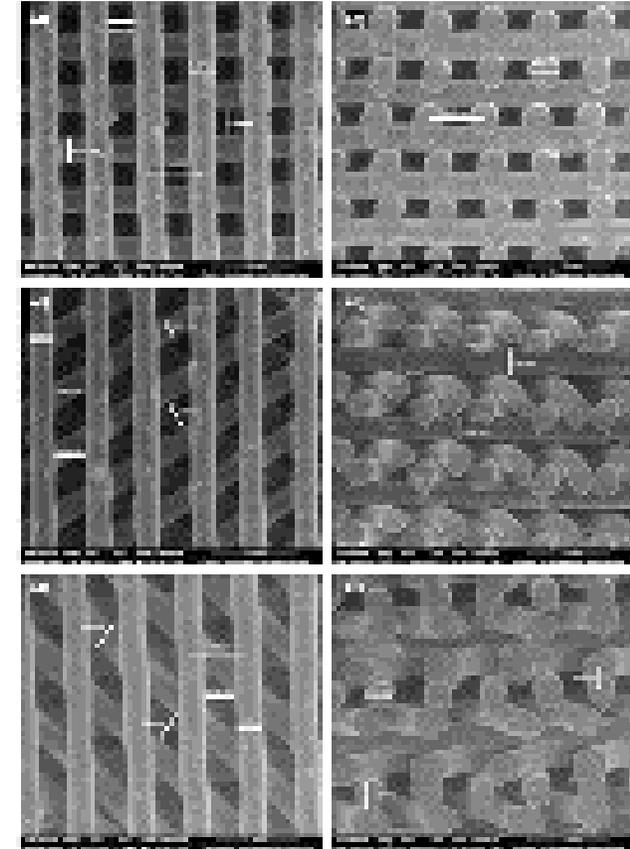
- 3D printing based on nozzle-deposition system
- Polymer solutions (solvent!)
- 3mm/s, 5 bar
- 500 μm between 70 μm struts
- Get the right set of temperature/plastiziser/printing parameters
- Post-processing : **shrinkage** of struts during solvent evaporation !!
- Hydrogels : + in-situ crosslinking and **swelling** : final resolution !



Melba Navarro, 2013, IBEC Barcelona

Additive manufacturing : molten polymer + composites

- **Polymers and composites :**
 - less shrinkage,+ higher viscosity, + higher mechanical properties
 - + different degradation rates
- **'Bioextruders' :**
 - deposition velocity (volume, nozzle diameter), with or without screw, pumping
- **Each constituent material requires specific processing conditions**
- **Access to the design freedom of the composite, multi-material deposition**
- **Bulk and surface properties**
- **Thermoplastic scaffold and bioactive hydrogel**



P.Bartolo, 2013

- **Custom-made 3D structures**
 - Reproduce geometry of body parts, surgeon support, replica of in vivo milieu
- **In vitro platforms to study cell response and drug screening**
 - scaffold pore size, geometry, wettability, adhesion, mechanical loading on cells behavior
- **Templates/scaffolds for tissue regeneration**
 - Building inner architecture and surface properties
 - Mechanical performance, permeability, nutrients diffusion, cell response...

Conclusions

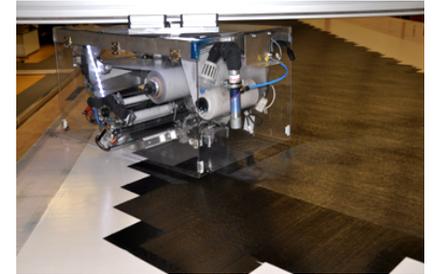
Building up from mm scale : 0.1-10 mm

- **Processing fibre composite today**
 - Tape and tow directional placements
 - Towards thinner ply (2-3 fibre thickness)
 - Towards 3D shape in cost-effective one-step process

- **Additive processing**
 - of laminate (ply by ply)
 - tow composite (placement and overinjection)



Spread Tow



Tape placement

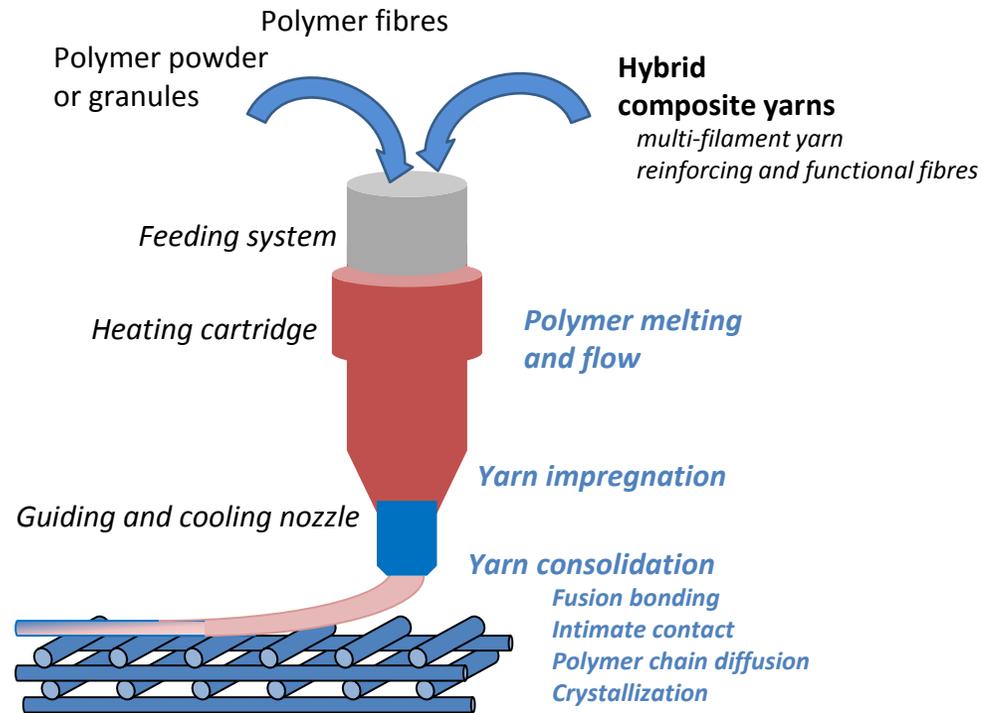
www.thinplytechnology.com



www.eelcee.com

www.inxide.se

Building up from μm scale : 5-200 μm

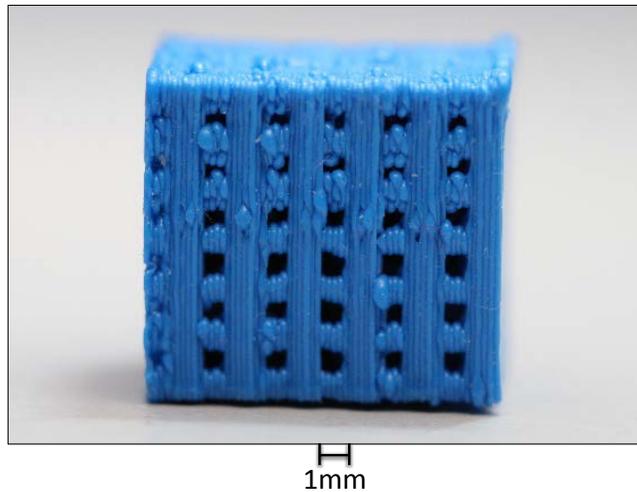


Fibres
Hydrogels
Resorbable polymer and biocomposites
Bio-performance

**3D cellular biocomposites
for implants, cells platforms
and degradable devices**

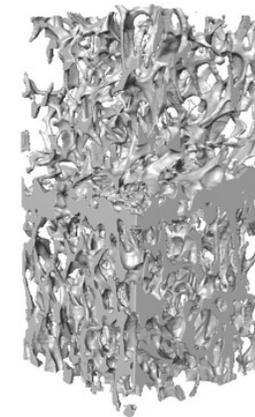
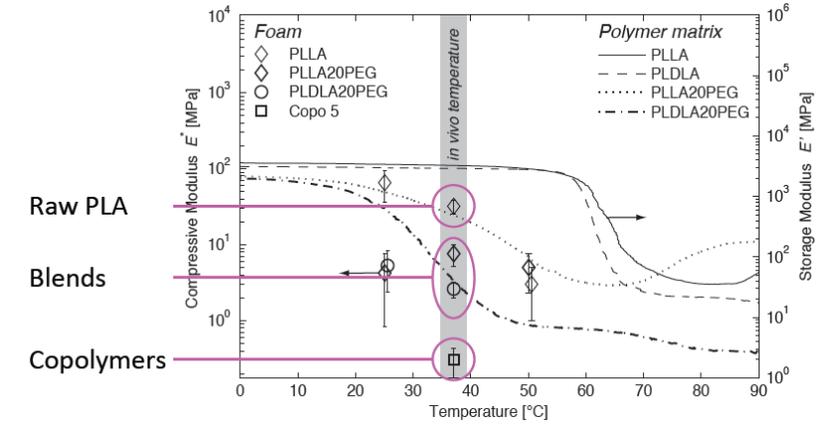
Building up from μm scale : 5-200 μm

1. 3D deposition for main scaffold
2. Impregnation with bioactive hydrogel
3. Post processing (crosslinking, ...)



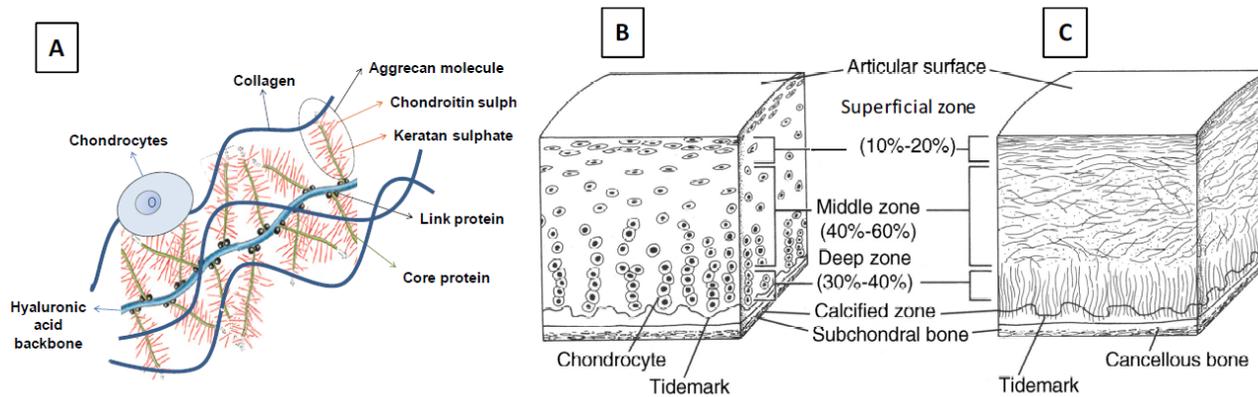
LTC-LBO SNSF project

- **Processing with single fibres**
 - not only at yarn level
 - control fibre properties during processing of implant
- **Processing 3D biocomposite**
 - be hybrid, anisotropic and bioactive

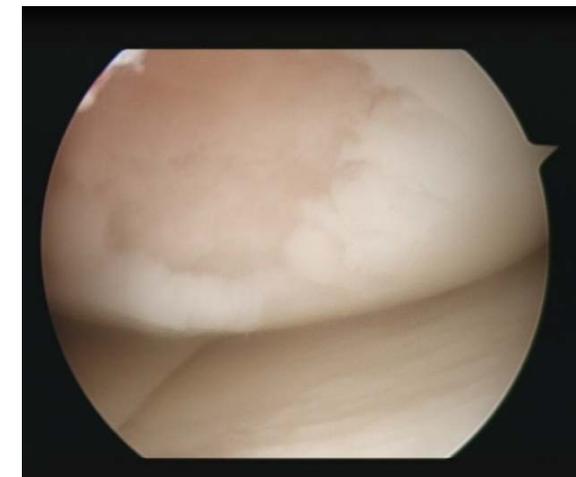


Cartilage

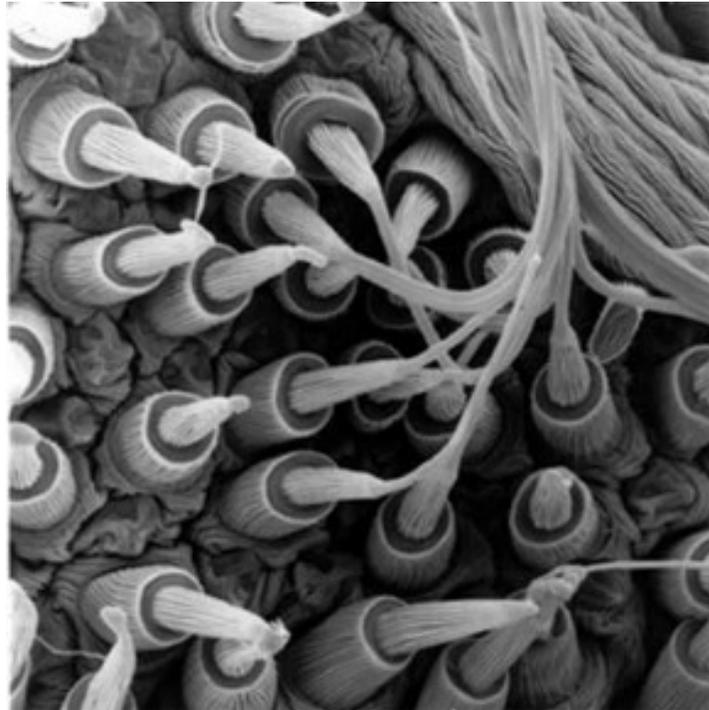
Bone



J.Izadifar *et al*, *Funct. Biomater.* 2012, 3 799



mykneecartilage



MicroAngela

AM: from Biomaterials to Regenerative Medicine

- **Swiss Society of Biomaterials and Regenerative Medicine**
- **20th Anniversary in 2015**
- **Conference at EPFL, June 9th and 10th 2015**
- **Biomaterials, Biofabrication, Tissue Engineering**

London museum of science



Merci

- EPFL-LTC
- EPFL-LBO, EPFL-LAPD
- CHUV
- SNSF, CTI, FP7
- Eric Boillat
- YOU