



Photocurable resin for 3D Printing

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Agenda

- What is AM (3D Printing)
- Usage of 3D Printing and its market
- Photocurable resin for 3D Printing
 - Vat Photopolymerization (Stereolithography)
 - Current special application
 - Material Jetting technology
- Nanoparticle for 3D Printing
 - Ceramic 3D Printing
- Summary

YNU Additive Manufacturing ; AM = 3D Printing

- Fabricate physical objects directly from 3D CAD data
- Materials, such as "Photo curable resin", "Plastic powder", "Plastic wire", "Plaster", "Paper" or "Metal powder".
- Accumulate layer by layer
- By using laser beam, electron beam, heat, Inkjet, etc.



YNU Typical Application by 3D Printing

- Verification Model, Functional Model, Assembly Model
- Rapid Prototyping
- Molding Die Design
- Small Lot Production (Aircraft parts etc.)



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Classification of 3D Printing Technology

| Additive technology | Common name | Material | Method, Equipment | Characteristics | Typical example |
|--------------------------------------|--------------------------|------------------------------------|------------------------------|--|---|
| Vat Photo polymerization (VPP) | Stereolithography SLA | Photocurable resin | LASER, LED | Precise, Accurate Big size | Prototyping Jewelry |
| Powder Bed Fusion (PBF) | SLS, SLM, EBM HSS | PA12, PP powder Metal powder | LASER, EB InkJet/Heating | Real parts (PA12) Metal parts | Aircraft parts, Metal parts, Injection Mold |
| Material Extrusion (MEX) | FDM, FFF | ABS, PC | Heating | Easy to use PLA ~Super Eng. Plastics | Prototype, Parts, Hobby |
| Binder Jetting (BJT) | InkJet, Z-Printer | Plaster powder Aqueous binder | InkJet | High speed Full color | Figure, 3D image |
| Material Jetting (MJT) | PolyJet MJM, ProJet | Photocurable resin Natural wax | InkJet | Various expression | Medical, Figure |
| Sheet Lamination (SHL) | LOM | Paper, Plastic, Metal sheet | LASER, Cutter knife | Easy to use Full color | 3D map |
| Directed Energy Deposition (DED) | LENS, DED | Metal powder | LASER | High speed | Metal parts |
| Hybrid | | Metal powder Resin wire, pellet | LASER + CNC Heating + CNC | Accurate Product level | Metal parts Plastic parts |

ASTM: 7 types + hybrid \rightarrow 8 types

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Industrial 3D Printer (>\$5,000)



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YNU Desktop (Personal) 3D Printer (<\$5,000)



Mini W+/XYZ

\$ 300



BONSAI mini/ \$1,000

Ultimaker

Ultimaker2+

\$3,000~



Form2+/SLA \$3,000~

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Car industry

Aircraft, 15.9% Aerospace

16.0%

14.4%

Academic



Desktop/Personal: <5,000\$: 753,000 http://www.wohlersassociates.com

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\$1.500

Makerbot/Replicater

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Usage of 3D Printing

Military

Power/ Energy

Home appliance

- Design verification and prototyping for production development
- High value-added industrial final products Construction Others
- Aircraft, aerospace industry
- Jewelry
- Medical and Dentistry
- Human body varies greatly from person to person, 3D printing is suitable for individual dimensions.
- Consumer goods
- Custom design, Art, Personal expression, Hobby



6.0%3.4%

10.9% 6.8%

13.9%

12.7%

Wohlers Report 2021

YNU Usage of Each 3D Printing Technology

| Usage | Purpose | Material | Process | Typical Manufacturer |
|----------------------------|----------------------------|-------------------------------------|------------------|---|
| | | Plaster | BJT | 3DSystems |
| | Verification model | Photocurable-resin | VPP, MJT | 3DSystems, CMET, D-MEC, DWS, Stratasys, 3DSystems, KEYENCE |
| | | Thermoplastics (Powder, wire) | PBF, HSS, MEX | EOS, 3DSystems, HP, Stratasys |
| Prototype | | Sheet (paper, PVC sheet) | SHL | MCor |
| | | Photocurable-resin | VPP | 3DSystems, CMET, D-MEC(JSR) |
| Functional test Fitting | Functional test Fitting | Thermoplastics (Powder, wire) | PBF, MEX | EOS, 3DSystems, Aspect, Stratasys |
| | | Metal powder | PBF | EOS, 3DSystems, SLM, etc |
| | Mold, casting pattern | Photocurable-resin | VPP | 3DSystems, CMET, D-MEC |
| Tooling (Mold) | ng d) Metal mold | Metal powder | PBF | Matsuera, SODICK |
| () | Sand casting mold | Natural Sand | BJT | ExOne, voxeljet, CMET |
| | Plastic product | Thermoplastics (Powder, wire) | PBF, MEX, HSS | EOS, Stratasys, HP |
| | Metal product | Metal powder | PBF, DED, Hybrid | EOS, 3DSystems, Matsuera, GE Additive |
| Final | Dental application | Photocurable-resin, Metal powder | VPP, PBF | DWS, EnvisionTEC, RapidShape, EOS |
| products | Metal mold | Metal powder | PBF | Matsuera, SODICK, DMG/Mori |
| BiO-3DPr | BiO-3DPrint | Bio ink, iPS cell | MEX | CELLINK, Cifuse, EnvisionTec |
| | Implant | Metal powder, PEEK, PEKK | PBF | ARCAM, EOS |
| Others | Fixture | Thermoplastics (Powder, wire) | PBF, MEX | EOS, Stratasys, Ricoh |
| Others | Education | Thermoplastics, Plaster | MEX, BJT | RepRap Machine, 3DSystems |

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W/W Market of 3D Printing (Wohlers Report 2021)



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Materials for 3D Printing



| Method | Manufacturer | | Materials | Application/Usage |
|---------------------|-------------------|----------------|----------------------------|-------------------|
| Wiethou | | Category | Classification | Application/Osage |
| VPP/LASER | 3D Systems | Photo-Resin | EPOXY / Acrylate Hybrid | RP |
| | CMET | Photo-Resin | EPOXY / Acrylate Hybrid | RP |
| | DWS | Photo-Resin | (Urethane) Acrylates, | Jewelry, Dental |
| | Formlabs | Photo-Resin | (Urethane) Acrylates | Hobby |
| VPP/DLP-lamp | Envisiontec | Photo-Resin | (Urethane) Acrylates | Jewelry, Dental |
| | ASIGA | Photo-Resin | (Urethane) Acrylates | Jewelry, Dental |
| Material Jetting | 3D Systems | Photo-Resin | (Urethane) Acrylates/Wax | Jewelry, Dental |
| | Objet (Stratasys) | Photo-Resin | (Urethane) Acrylates | Model, Dental |
| | 3D Systems (Z) | Plaster | Plaster/Water | Design |
| | Solidscape | Wax | Wax+Polyester binder | Jewelry |
| PBF/LASER | EOS | PA, Metal P | PA12, SUS, Ti, Al, Co-Cr | RP. Prod, Medical |
| | 3D Systems | PA, Metal P | PA12, SUS, Ti, Al, , Co-Cr | RP. Prod, Medical |
| | ASPECT | PA, PP | PA12, PP | RP |
| PBF/EBM | ARCAM | Metal P | Ti (alloy) | Medical(Implant) |
| Materials Extrusion | Stratasys | Thermoplastics | ABS, PC, PEI, PPSF etc | RP, Model |
| | 3D Systems | Thermoplastics | ABS, PLA | Model, Hobby |
| | RepRap etc. | Thermoplastics | PLA | Hobby |

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3D Printing using Photocurable Resin

1. Vat Photo-polymerization (VPP)

YNU 3D Printing using Photocurable Resin



| | Large size LASER | Small size LASER | DLP | InkJet |
|--------------|------------------|--|--|--|
| | Free surface | Regulated surface | Regulated surface | Photocurable resin |
| | (VPP) | (VPP) | (VPP) | (MJT) |
| Light source | UVLASER | LD LASER | LED, UV lamp | |
| (nm) | 355nm | 405nm | Vis. lamp、 405LED | UV lamp |
| Process | Contact with air | Transparent window Not contact with air | Transparent window Not contact with air | InkJet Contact with air |
| T · 1 | 3D Systems | DWG | EnvisionTEC | Stratasys |
| Typical | CMET | DWS Familalia | ASIGA | KEYENCE |
| Manufacture | D-MEC | Formlabs | Nexa3D | 3D Systems |
| Scheme | | Working table Resin tank | ID-object | Anting Head Xank Yank Factors # Factors # Guern Factors And Tay Xank |
| | D.4 | | | 13 |

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Example of VPP Machine



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YNU VPP (stereolithography) Process Video



Free Surface VPP Scheme

From CMET Inc., HP



Typical Application of VPP





Prototyping of car dashboard/SOLIZE



Functional testing model



Silicone molding with polyurethane



Casting pattern and casting by SUS

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YNU Properties of Photocurable Resin for VPP



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| | ABS Resin | TSR- | 884B | Accura Xtreme | Figure4 Tough 65C BLK | Formlabs Grey Pro | Henkel Loctite IND403 |
|--|--------------|---------------|---------------|-----------------------|-----------------------------|----------------------|--------------------------|
| Manufacturer | | CM | IET | 3DSystems | 3DSystems | Formlabs | Henkel |
| Method | | Free s LAS | urface SER | Free surface LASER | Regulated DLP | Regulated LASER | Regulated DLP |
| Base Resin | | Epoxy/A | Acrylates | Epoxy/Acrylates | UA. | UA | UA |
| Viscosity(mPa•s)(25°C) Sp. gravity (25°C) | 1.04 | 60 1. | 00 10 | 250~300/30°C 1.13 | 1900 1.13 | | 100~200 1.08 |
| Post Treatment | | UV | 120°C | UV | UV/60~90°C | UV/80°C/120m. | UV, <80°C |
| Tensile Strength (MPa) | 43 | 51 | 50 | 38~44 | 41 | 61 | 87 |
| Elongation (%) | 15~60 | 3~12 | 4 | 14~22 | 35 | 13 | 8.5 |
| Tensile Modulus (MPa) | 1,800 | 2,370 | 2090 | 1790-1980 | 1700 | 2600 | 2750 |
| Flexural Strength (MPa) | 70 | 87 | 79 | 52-71 | 60 | 86 | 91 |
| Flexural Modulus (MPa) | 2,250 | 2,260 | 2260 | 1520-2070 | 1600 | 2200 | 2900 |
| Izod (J/m, noched) | 200 | 30 | 25 | 35-52 | 31 | 18.7 | 27 |
| HDT (°C)/ 1.8MPa | 80~100 | 53 | 100 | 54 | 51 | 62.4 | 64.7 |
| HDT (°C)/0.45MPa | | 58 | 117 | 62 | 70 | 77.5 | 81.7 |
| Surface hardness (ShoreD) | | 87 | 86 | 86 | 81 | | 80 |
| Water absorption (%) | 0.3~0.4 | 0.4- | -0.5 | 0.5~0.7 | 0.62 | 0.83 | - |

Each data is taken from manufacture's website; UA: Urethane Acrylate

YNU Summary of Vat Photo Polymerization (VPP)

- VPP gives most accurate and transparent model.
- Customer requests high HDT, highly durable products same level as engineering or super engineering plastics, At most ABS resin level: HDT > 80°C, durable



Highly transparent resin TSR-829/CMET



Current Status of VPP Resin

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Current effective applications



• Invisalign: Flow of Orthodontics (from HP)

1. Consultation for patient



2. Planning with 3D CAD



3. Fabrication of aligner



- Aligner is obtained with PC film by Compression modeling using VPP model
 - 4. Start treatment



Already treated for more than 40 million people.

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3D P

2005

YNU Jewelry Application/DWS Italy





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YNU Dental Application/DWS Italy





3D Printing with Photocurable Resin

2. Material Jetting with Photopolymer

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YNU 3D Printing using Photocurable Resin



| | Large size LASER Free surface (VPP) | Small size LASER Regulated surface (VPP) | DLP Regulated surface (VPP) | InkJet Photocurable resin (MJT) |
|------------------------|---|--|--|--|
| Light source (nm) | LASER 355 | LD LASER 405 | LED, UV lamp Vis. lamp、 405LED | UV lamp |
| Process | Contact with air | Transparent window Not contact with air | Transparent window Not contact with air | InkJet Contact with air |
| Typical Manufacture | 3D Systems CMET D-MEC | DWS Formlabs | EnvisionTEC ASIGA Nexa3D | Stratasys KEYENCE 3D Systems |
| Scheme | | Working table Resin tank | 3D-object | Series I was Factor Re- Factor Re- Relations Re- Built Tay |



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YNU Photocurable resin with Material Jetting





Nano particle for 3D Printing

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YNU History of nanoparticle filled resin

1994~2003

T. Hagiwara et al., : Urethane acrylate-based photocurable resin with glass beads, silica particles, inorganic whiskers, etc. to strengthen the mechanical properties;
Filler content: ~ 50 wt%

High HDT and high rigidity: > HDT 250 °C > 10 GPa

1996 M.L. Griffith et al .: Water-based photocurable slurry resin

- 2000 JSR was followed with silica / epoxy based resin
- And SOMOS and 3D Systems also followed





2000~

- OPTOFORM system by Dr. Andre-Luc Allanic, Nancy, France Sold to 3D Systems, but 3D Systems abandoned to sell in the market.
- More than 10 units were sold in EU.
- The technology was taken over by 3D Ceram in France.
 Resin composition: Resin + Fillers (20% ~ 62% Vol.)

YNU Nanoparticle filled Photocurable VPP resin



| Manufacturer | Filler | Content | Base resin | Item |
|---|---|----------|---------------------------|--|
| Teijin Seiki/CMET (TSR-745, 755) | Spherical nano silica/Barium titanate whisker | ~50wt% | Special urethane acrylate | High rigidity, high heat resistance, mold, special parts |
| JSR (SCR-801, 802) | Spherical nanoo silica | ~35wt% | Epoxy/Acrylate hybrid | Excellent surface quality, mold |
| DSM-SOMOS (from JSR) (SOMOS PerForm, Nanotool) | Spherical nano silica + α | 35~40wt% | Epoxy/Acrylate hybrid | Wind tunnel test parts, F-1 prototype, special parts |
| 3DSystems (Accura Bluestone) | Spherical nano silica + α | 40~45wt% | Epoxy/Acrylate hybrid | Wind tunnel test parts, F-1 prototype, special parts |











SOMOS PerForm



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YNU Current Ceramic 3D Printing Materials

| E | |
|---|--|
| | |

| Manufacturer | Method | Materials | Ceramic content | Ceramic | Typical application |
|----------------|------------------------|--|-----------------|---------------------------------|--|
| Lithoz | VPP/Slurry | Ceramic powder /UA photocurable resin | ~50wt% | Alumina, Zirconia, SiN, βTCP | Ceramic parts, Medical |
| Admatec | VPP/Slurry | Ceramic powder /UA photocurable resin | ~50wt% | Alumina, Zirconia | Ceramic parts, |
| 3DCeram-Shinto | VPP/Paste | Ceramic powder /UA photocurable resin | >50vol% | Alumina, Zirconia, HAP | Ceramic parts, |
| SK-Fine | VPP/Slurry | Ceramic powder /UA photocurable resin | 65~70vol% * | Alumina, Zirconia, Zeolite | Investigating |
| DWS | VPP/Slurry | Ceramic powder /UA photocurable resin | ~50wt% | Silica, Alumina Zirconia | Artificial teeth, Artificial Jewelry |
| DLP machines | VPP/Slurry | Ceramic powder /UA photocurable resin | 20~50wt% | Silica, Glass beads | Dental model |
| NanoE | MEX/Wire | Ceramic powder/PLA resin | >50vol% | Alumina, Zirconia | Ceramic parts, |
| Daiichi Ceramo | MEX/Pellet | Ceramic powder/Thermoplastic resin | 80wt%, 50vol% | Alumina, Zirconia | Ceramic parts, |
| AIM3D | MEX/Pellet | Ceramic powder/Thermoplastic resin binder | ? | Alumina, Zirconia, SiN | Searching |
| WASP, WZR etc. | MEX/Cray | Cray | ? | Cray | Pottery |
| voxeljet | BJT/Powder | Ceramic powder/ Resin binder | ? | Cooperate Johnson Matthey | Car parts |
| ExOne | BJT/Powder | Ceramic powder/Resin binder | ? | SC, Alumina, Zirconia, BC | Car parts, Medical |
| 3DSystems | BJT/Powder | Ceramic powder/water soluble binder | ? | TCP (Next21) | Medical (Born) |
| Kwambio | BJT/Powder | Ceramic powder/water soluble binder | ? | ? | |
| XJet | MJT/Suspensi on | Ceramic nano particle/binder | 60vol% | Alumina, Zirconia, HAP | Ceramic parts, Medical |
| OsseoMatrix | PBF/LASER/ Powder | Ceramic powder/ Resin coating | ? | НАР | Medical (Born) |
| nScrypt | MEX (Microdispense) | Ceramic suspension ? | ? | | Medical etc. |



driven by application revenues and hardware revenues. Source: SmarTech Publishing



Ceramic 3D Printing Systems



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YNU Ceramic 3D Printing by MEX/NANOe



YNU Ceramic 3D Printing by MJT/XJet



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Typical Application by Lithoz



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| | LithaLox HP 500 | LithaCon 3Y 210 | LithaNit 720 |
|--------------------------|--------------------|-----------------------------|-----------------------|
| Powder composition | 99.95% Al2O3 | 3 Mol% Y2O3 stabilized ZrO2 | >90% Silicone Nitride |
| 4 point bending strength | 430 MPa | 935 MPa | 760 MPa |
| Density | > 99.4% T.D. | > 99.8% T.D. | > 99.6% T. D. |
| Surface roughness | $\sim 0.4 \ \mu m$ | <1.0 µm | $\sim 0.7 \mu m$ |



LITHOZ

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Material Portfolio



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DCERAM

YNU Typical Application by 3D Ceram

Broadening the use of Technical Ceramics with 3D printing



Alumina



Hydroxyl apatite

- Alumina, Zirconia, Hydroxyl apatite
- Density after firing: 99.7% or more
- Electric parts, Medical parts

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| Company | Machine | AM- approach | Qualified Material Offerings |
|----------------------|--------------------------|---------------------|--|
| Admatec BV Europe | Admaflex | P _{poly} | Al ₂ O ₃ , ZrO ₂ , SiO ₂ , ATZ, SiO ₂ -sand |
| Lithoz GmbH | CeraFab | P_{poly} | Al ₂ O ₃ , ZrO ₂ , Si ₃ N ₄ , SiO ₂ , TCP |
| 3DCeram | Ceramaker | \mathbf{P}_{poly} | Al ₂ O ₃ , ZrO ₂ , ATZ, |
| Xjet | Carmel | Mjet | ZrO_2 , Al_2O_3 * |
| Johnson Matthey | PixDro | Bjet | Al_2O_3 |
| ExOne | M-flex, Innovent etc. | Bjet | ZrSiO ₄ , Al ₂ O ₃ , & SiO ₂ foundry sands |

Table 1. Commercial monolithic AM ceramic solutions available to the U.S. market. *Note:** Xjet Al₂O₃ was announced in Nov. 2018.

Jessica Schiltz et al. / Procedia Manufacturing 34 (2019) 780-788

| Table 3. AM vendor processing parameters. Particle size was notably smaller |
|---|
| for P_{poly} vendors compared to Bjet, but solids loading was equivalent. $n = 3$ |
| for all vendors except Mjet, $n = 2$. Specific binders could not be provided. |

| Vendor | Matl. | Particle Size | Sintering | | Solids loading | Layer thickness |
|----------------------------------|--------------------------------|------------------|-----------|------------------|-------------------|--------------------|
| | | μm | (°C) | (hr) | % | μm |
| P _{poly} 1 (Lithoz) | Al_20_3 | 0.05-1.0 | 1600 | 2 | 60 | 25 |
| | $Zr0_2$ | 0.05-1.0 | 1450 | 2 | 40-45 | |
| P _{poly} 2 (Admatec) | Al_20_3 | ~0.010 | ~1620 | 1 | 40-50 | 30 |
| | $Zr0_2$ | 0.090 | ~1525 | 1 | 40-50 | |
| Bjet (J. Matthey) | Al ₂ 0 ₃ | 40.0 | 1400 | n.r. | 50 | 100 |
| Mjet (Xjet) | Zr0 ₂ | 0.030 - 0.090 | n.r. | 12, one- step | 60 | 10 |

Jessica Schiltz et al. / Procedia Manufacturing 34 (2019) 780–788





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Summary



- Photocurable resins for 3D Printing are discussed
 - Vat Photo-polymerization
 - Material Jetting with photocurable resin
- Application and future are discussed.
- Nano particle is useful for 3D Printing.
 - 3D Printing is to be important for ceramic manufacturing.

