Three Decades of UV Technology Innovation: Stereolithography

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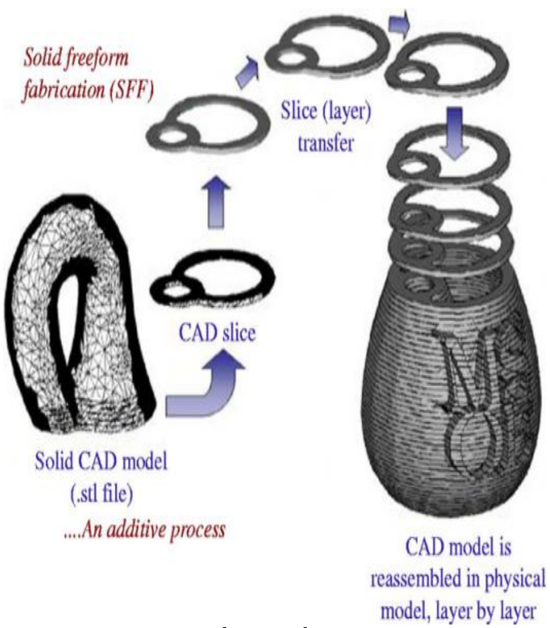
HEALTH · NUTRITION · MATERIALS

Outline

- Overview three decades of stereolithography
- Stereolithography Materials Innovations
  - The Foundation Years: 1984 - 1994
  - The Expansion Years: 1994 - 2004
  - The Diversification Years: 2004 - 2014
- Future of Stereolithography

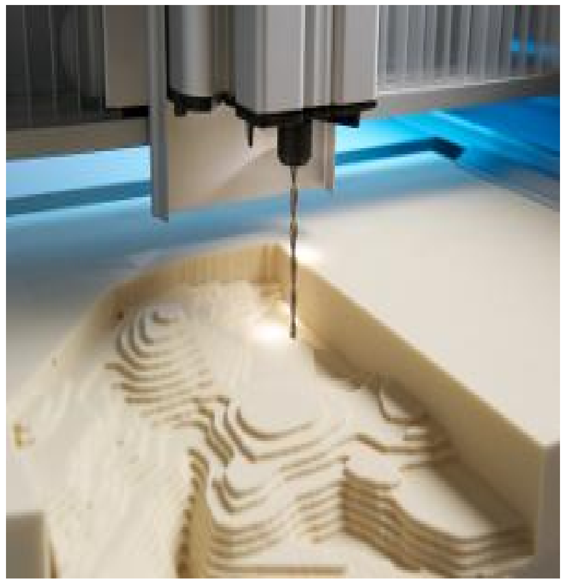
What is additive manufacturing?

Additive manufacturing
Build objects layer by layer



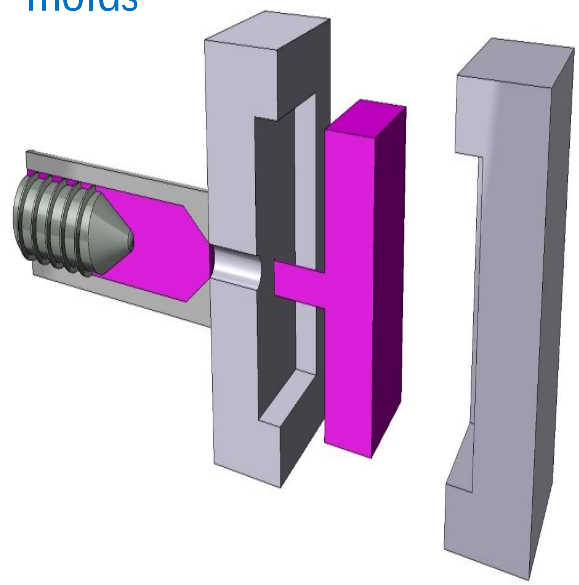
- Laser sintering
- Lamination, extrusion
- Ink-jet printing
  Stereolithography

Subtractive manufacturing
Cut away materials from a starting block



- Large waste materials
- Intensive cost and time
- Limited special configuration

Formative manufacturing
Forced material into the desired shape using molds



- Intensive cost and time
- Broad range of expertise
- Investment casting
- Injection molding
- Compressive molding

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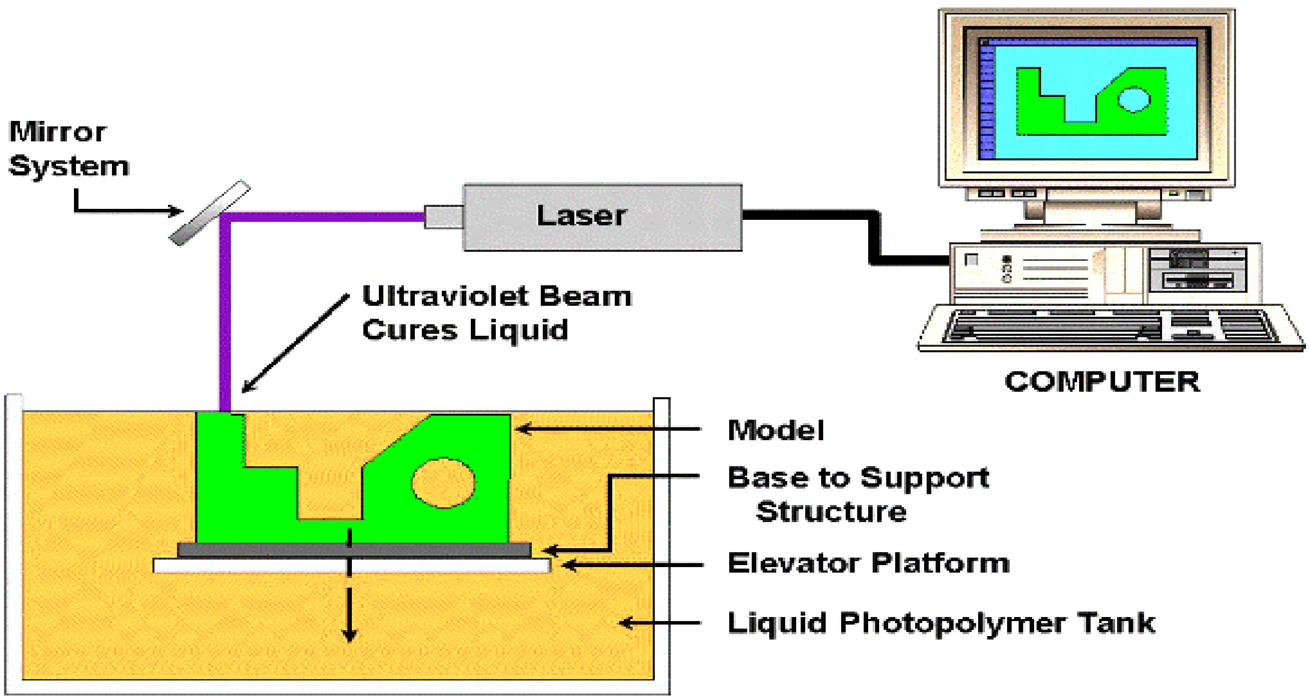
Stereolithography

Stereolithography builds shapes using light to selectively solidify photocurable resins layer by layer, replicates or creates any computer designed article into a solid 3-dimensional object within hours



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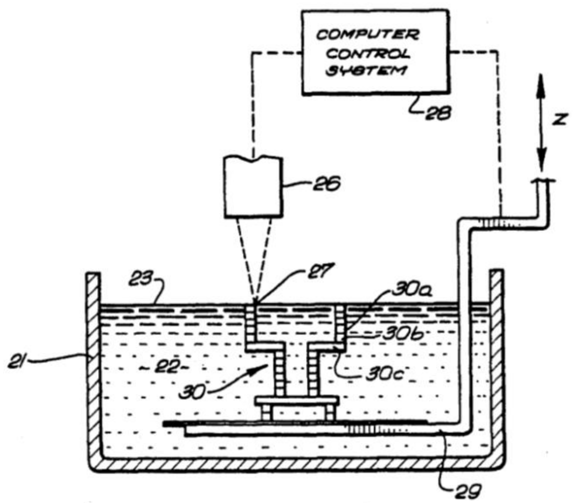
1986: The beginning of a new industry

- 3D Systems Inc. commercializes a new process
- Founder Chuck Hull coins term "Stereolithography"



Early 3D Systems SL Prototype

United States Patent [19]
Hull

[11] **Patent Number:** **4,575,330**
[45] **Date of Patent:** **Mar. 11, 1986**

[54] APPARATUS FOR PRODUCTION OF THREE-DIMENSIONAL OBJECTS BY STEREOLITHOGRAPHY
[75] Inventor: Charles W. Hull, Arcadia, Calif.
[73] Assignee: UVP, Inc., San Gabriel, Calif.
[21] Appl. No.: 638,905
[22] Filed: Aug. 8, 1984

4,252,514	2/1981	Gates	425/162
4,288,861	9/1981	Swainson et al.	365/127
4,292,015	9/1981	Hritz	425/162 X
4,329,135	5/1982	Beck	425/174
4,333,165	6/1982	Swainson et al.	365/127 X
4,374,077	2/1983	Kerfeld	264/22
4,466,080	8/1984	Swainson et al.	365/127 X
4,471,470	9/1984	Swainson et al.	365/127

Primary Examiner—J. Howard Flint, Jr.

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An innovation synergized other frontier technologies

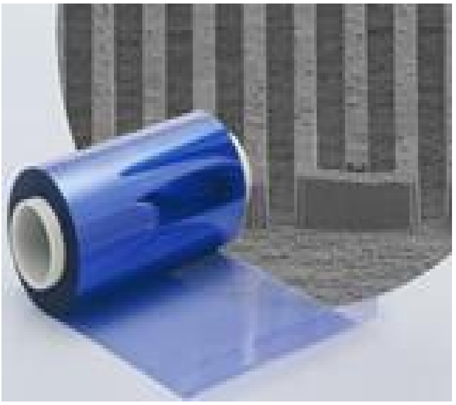
<u>Computer Technology</u>:
1980 Microsoft partnered with IBM
1980 Apple III released
1981 IBM PC went mass market

<u>Gas Discharged Laser Technology</u>:
1980s, Argon laser (351 nm): 1.5 Watt
1986, He-Cd Laser (325 nm): 2 mW

1958, DuPont® Dycril
1st photopolymer-based print plate for flexography

<u>Photopolymerization Technology</u>
1980s, Industry productivity significantly advanced by photopolymerization massive application in

- Flexography: Printing & publishing industry
- Photolithography: Semiconductor industry



1968, DuPont® Riston® 1st dry film photoresist revolutionized PCB fabrication methods

From Rapid Prototyping to Additive Manufacturing

- Most widely used AM technology
- Various SL equipment manufacturers and material suppliers globally

Materialise “Mammoth” (Belgium)

3D Systems, Inc. (Global)

UNIONTECH (China)

CMET(Asia)

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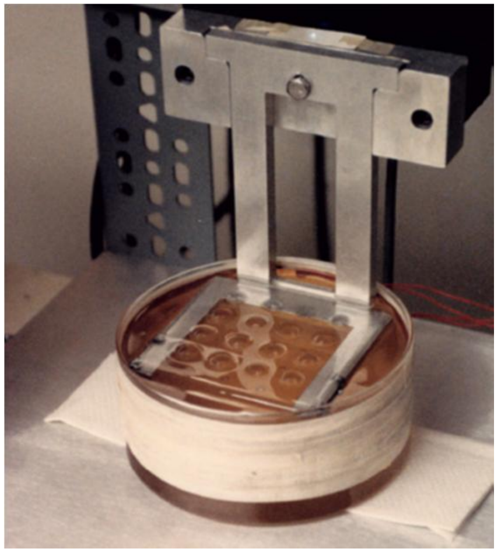
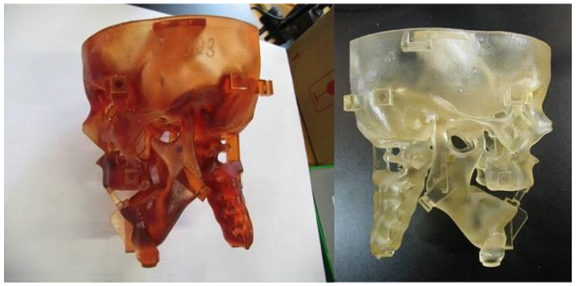
From Rapid Prototyping to Additive Manufacturing

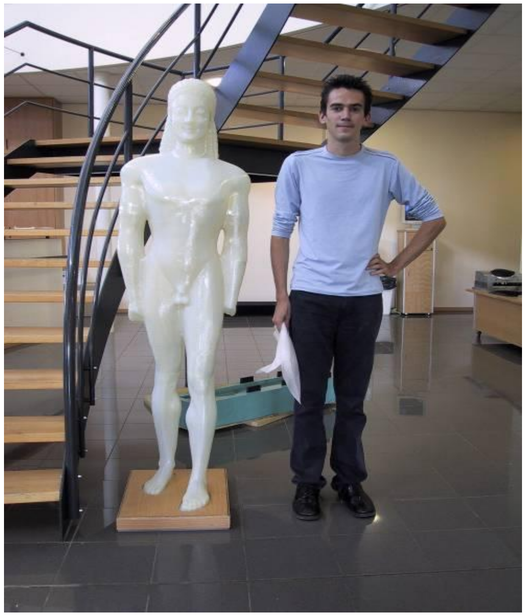


SL machine in DeSoto Lab



Acrylate parts
- High shrinkage
- Brownish color after aging

Life-size replica with Somos® 18420



Materialise machines
- Hold up to 1.5 metric ton of resin
- Produce full size statues, automobile dashboards

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From Rapid Prototyping to Additive Manufacturing

As materials, equipment, software and processing knowledge advanced, applications grew from concept and communication models, to fit and function testing, patterns, tooling and end use parts

Functional Testing

Tooling

Communication Models

Investment Casting Patterns

End Use Parts

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Drivers for Stereolithography growth

- Equipment: Speed, accuracy & size
- Laser capabilities
- Computing Power: Capabilities and cost
- Software development: Build styles and image scanning
- CAD: Cost and required skill level to operate
- Intellectual property
- Knowledgeable user community
- UV-curable photopolymer mechanical and physical properties

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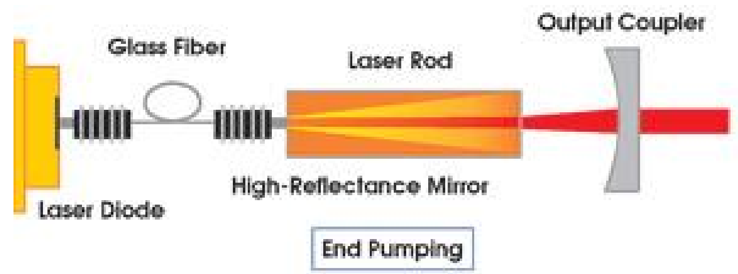
30 years of evolution in laser technology

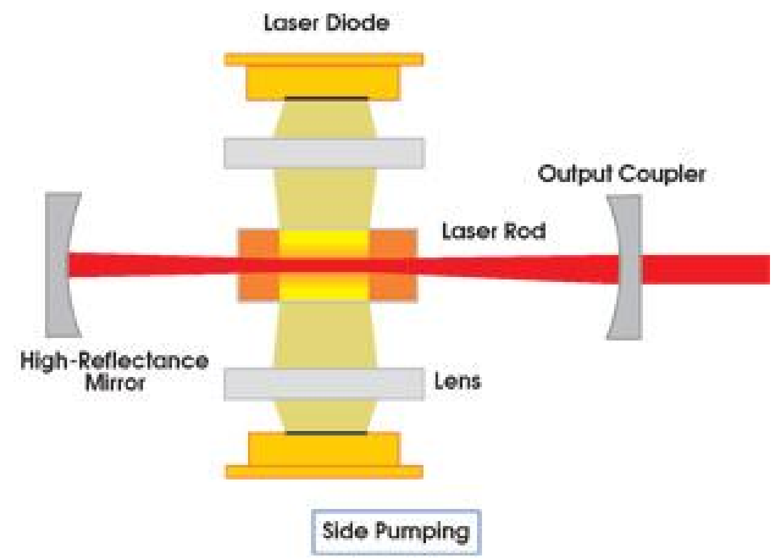
Solid state laser (355 nm):
1996: solid state laser began installing in SL system
1999: 700 mw was installed in SL-7000
2014: 1450 mw in ProJet® 8000 is available
7000 mw/10000 h available today

He-Cd laser (325nm):
20~40 mw output was installed commercially
100 mw/10000h life time available in 1990s

Argon ion laser (351 nm):
50~100 mw output was installed commercially
500 mw/2000h life time available in 1990s
7000 mw available today

Diode-pumped solid state laser





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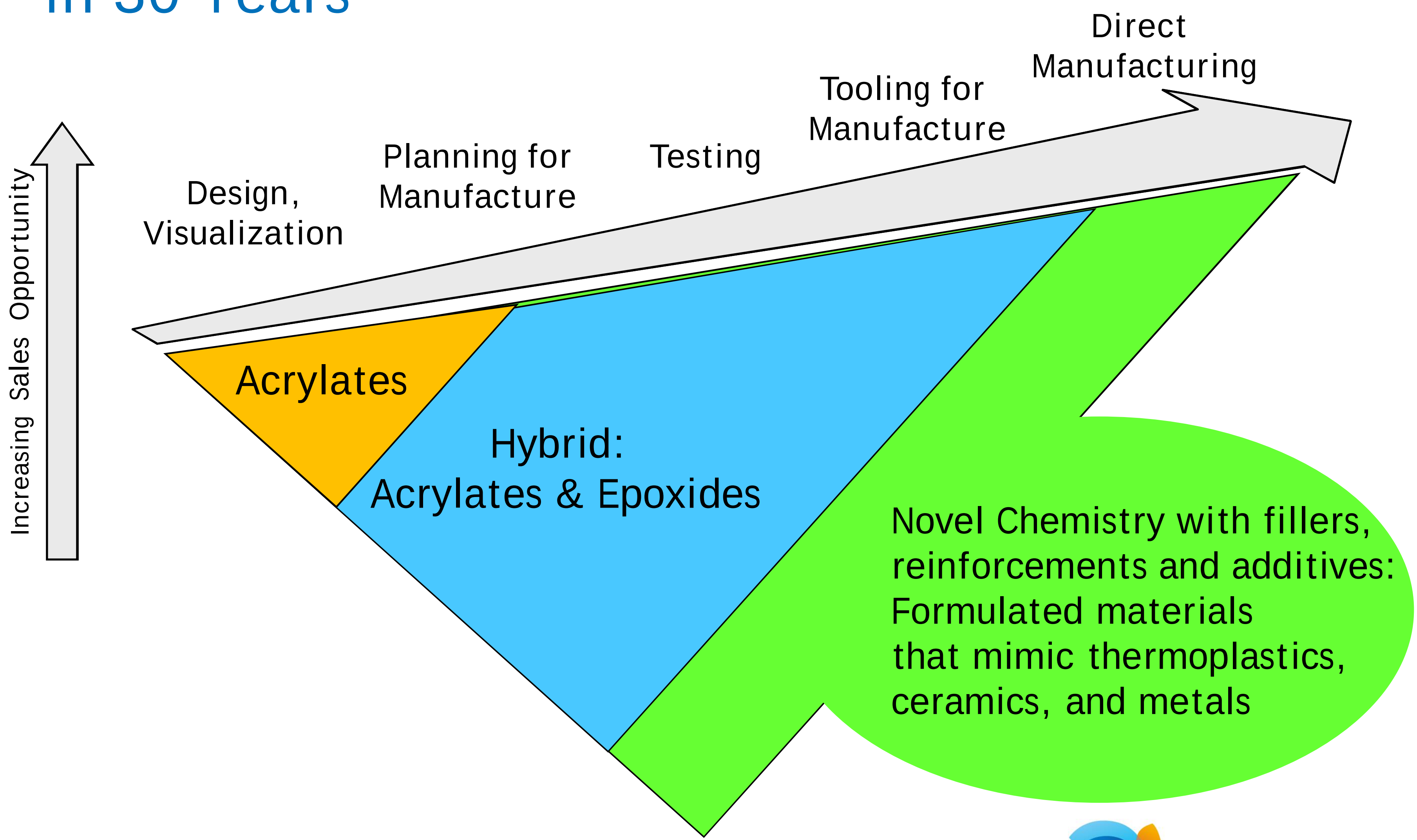
Market evolution of Stereolithography in 30 Years



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The Foundation Years: 1984-1994

Acrylate based formulations provided the required speed of reaction and overall cure properties for early SL

Challenges of historical acrylate based SL formulations:

- High liquid viscosity: ~ 2000 cps @ 30°C
- Problematic dimensional consistency: Shrinkage, curl and distortion
- Strength from laser cure: Laser power, SL resins and build style
- Brittleness: Acrylate chemistry, formulation skill and undercure

Assessing accuracy in SL parts

- 1990: Accuracy assessed by 170 dimensional checks performed on a standardized part geometry using a coordinate measuring machine
- H-4 Bar

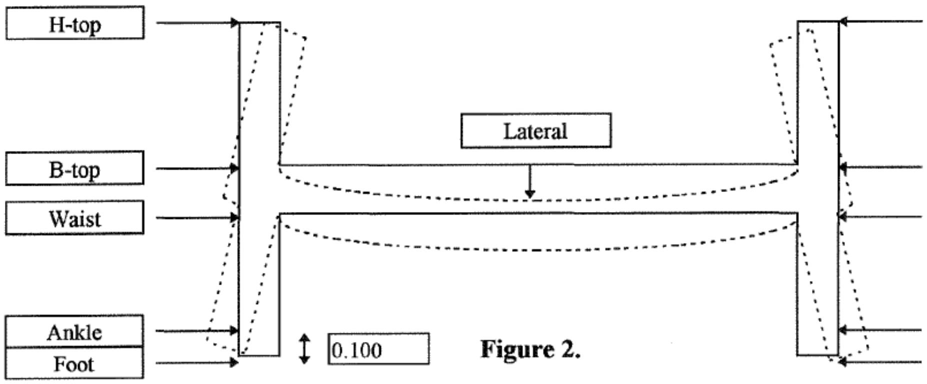
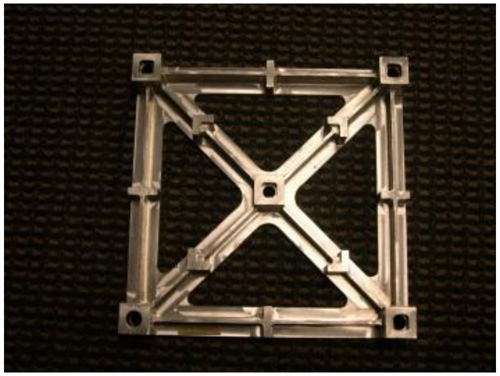


Figure 2.



SL user’s part

Distortion in vat: Shrinkage of lateral pulls in leg (at waist) — “dent” or “sink”

- Distortion after post support removal: lack of green strength can allow curling of lateral and “splaying” of legs once constraining supports are removed
- Shrink over postcure

Dr. Neckers' Vision on Stereolithography in 1990

CENTER FOR PHOTOCHEMICAL SCIENCES
LIGHTING THE WAY
BOWLING GREEN STATE UNIVERSITY

Vision on future SL

- Cationic photopolymerization
- Tailored to visible wavelength
- Medical applications

—Stereolithography: an introduction, Chemtech, 615-619, Oct. 1990.

Spectra Group Limited, Inc.

— Stephen G. Anderson, "Doug Neckers: Pioneer in Stereolithography". *SPIE Professional January 2013*

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Epoxide/Acrylates hybrid SL resins in 1993

Resin Type	Acrylate	Urethane Acrylate	Epoxy
Resin Name	XB 5081-1	XB 5149	XB 5170
Physical Properties			
Viscosity @ 30°C	2,400 cps	2,000 cps	180 cps
Green Flexural Modulus**	620 MPa	310 MPa	1700 MPa
Cured Tensile Modulus***	3,000 MPa	1,150 MPa	2,700 MPa
Elongation@Break***	2.5 %	10 %	9 %
Impact Strength***	3 kJ/m²	23 kJ/m²	30 kJ/m²

- Though slower in photospeed, epoxy/acrylate systems brought lower viscosities for easier processing and part cleaning
- Green strength and impact strength (or brittleness) were improved

Thomas Pang , "*Stereolithography Epoxy Resin development: Accuracy and Dimensional Stability* " ,
Proceedings of the 1993 North American Users Group Meeting, Atlanta, Georgia, March 1993

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Epoxide/Acrylates hybrid SL resins in 1993

Resin Type	Acrylate	Urethane Acrylate	Epoxy
Resin Name	XB 5081-1	XB 5149	XB 5170
Dimensional Properties and Accuracy			
UserPart Accuracy* (R.M.S. Error)	5.3 mils	6.1 mils	2.8 mils
Cantilever Curl*	10 %	10 %	1%
Green Creep Rate*	3.7 mil/$\log_{10}$ t	11.5 mil/$\log_{10}$ t	0.5 mil/$\log_{10}$ t
Linear Shrinkage	0.7 %	0.6 %	0.06 %
Flat Slab Distortion	71 mils	70 mils	20 mils

- Part accuracy improved based on reduced curl, shrink and distortion

Thomas Pang , "*Stereolithography Epoxy Resin development: Accuracy and Dimensional Stability* " , Proceedings of the 1993 North American Users Group Meeting, Atlanta, Georgia, March 1993

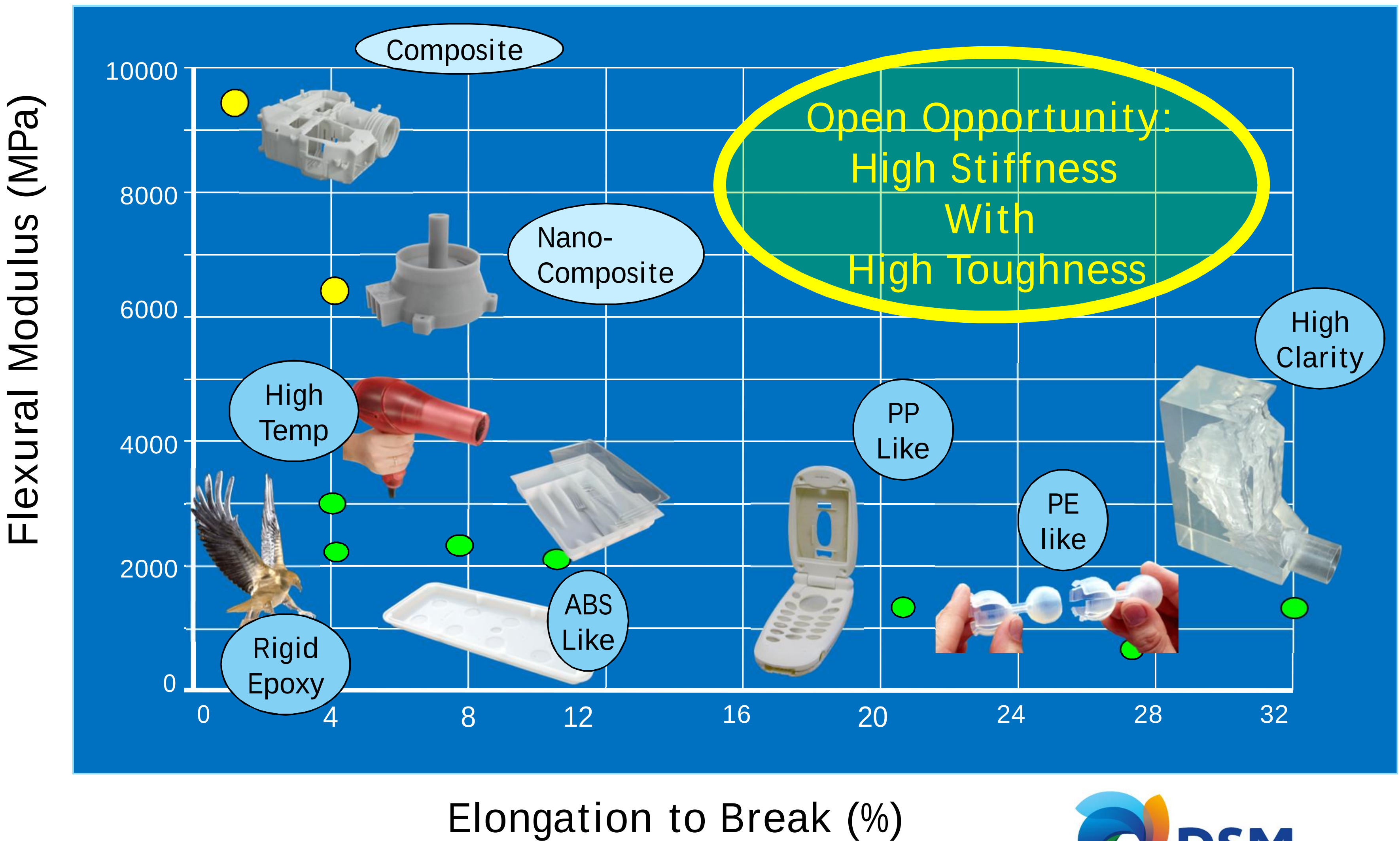
The Expansion Years: 1994 to 2004

- Epoxide/Acrylate hybrid system created SL materials that mimic many properties of thermoplastics:
  - Polyethylene, polypropylene and ABS
  - Combination of toughness and stiffness

- Clear, colorless materials expanded application capabilities in fluid flow behavior analysis

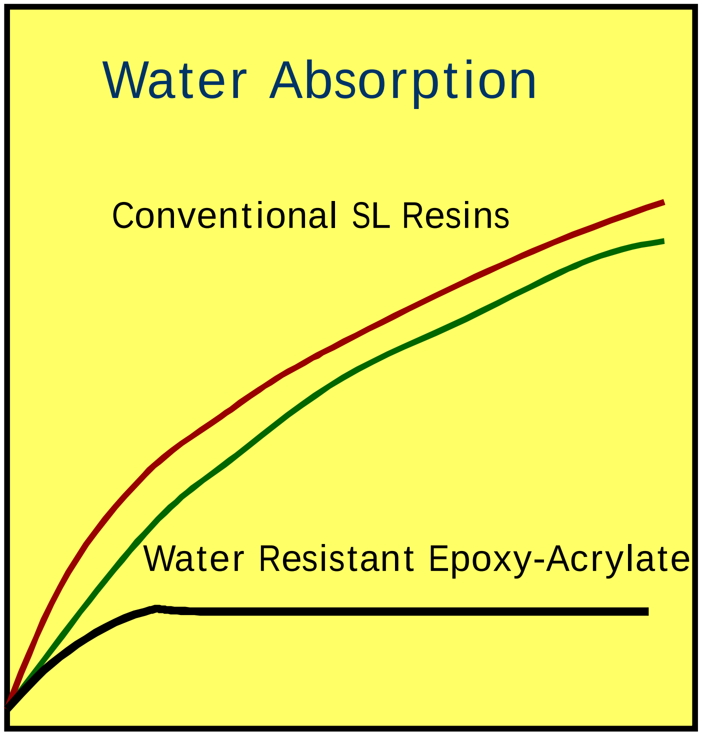
- Composite SL materials emerged, dramatically improving build accuracy, expanding range of strength, stiffness and temperature resistance

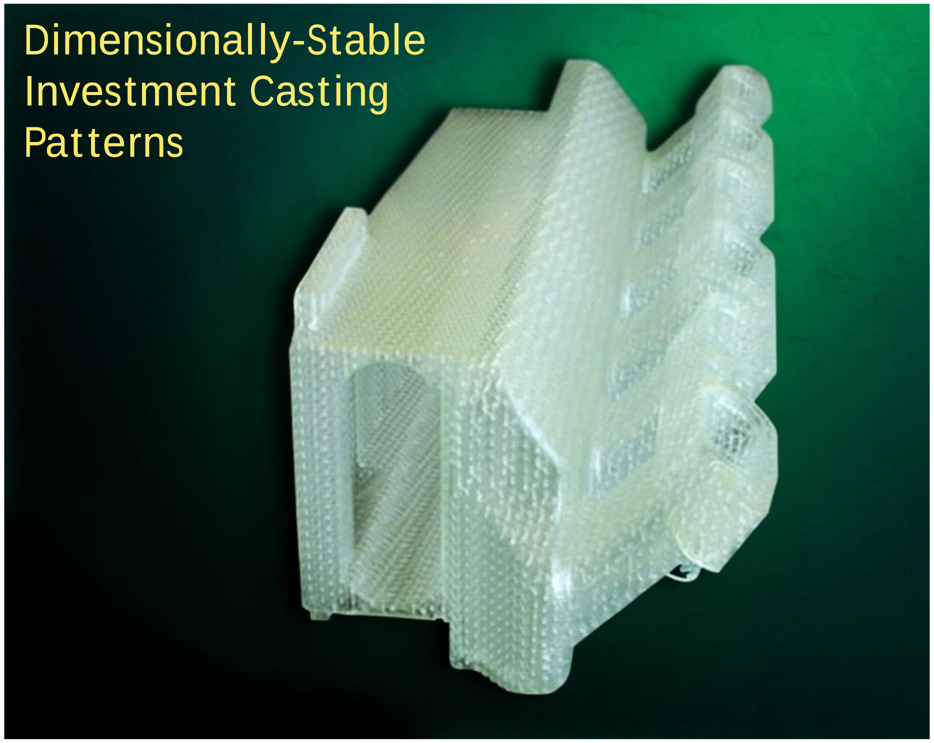
1994 - 2004: SL material capabilities expanded



1994 - 2004: SL applications grow in size and diversity

- Hollow SL parts for patterns for investment casting of metals first introduced with hybrid SL materials in 1993
- Next generation hybrid SL resins further enhance dimensional stability





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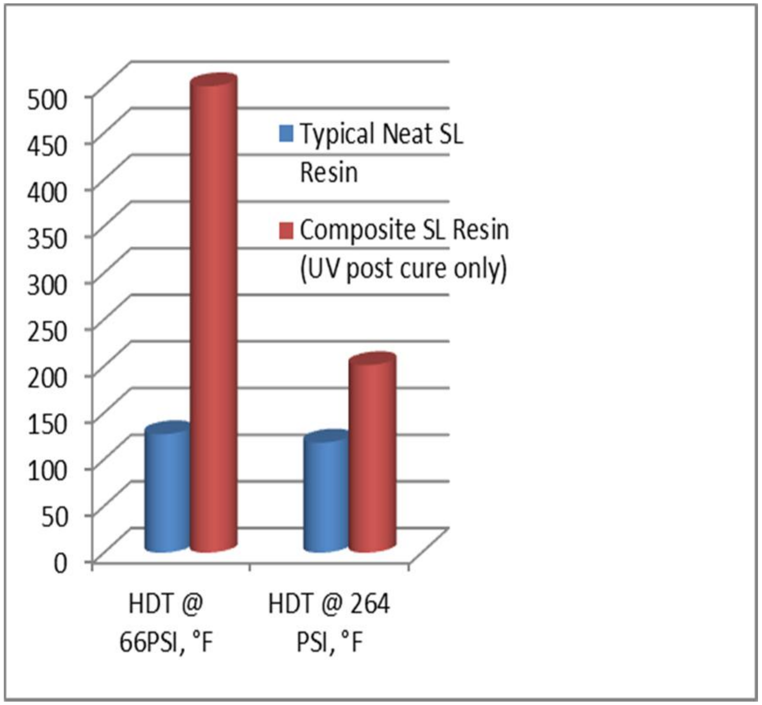
1994 - 2004: SL applications grow in size and diversity

Composite SL materials heat resistance, low shrinkage and lower thermal expansion , compared to neat SL materials opened novel rapid tooling applications



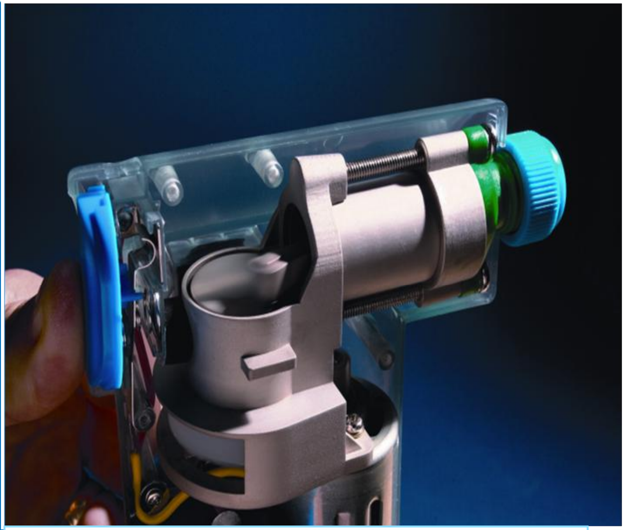
Injection Molding: Temperature resistance, strength and accuracy

1994 - 2004: SL applications grow in size and diversity

Composite SL materials providing low water absorption and excellent dimensional stability facilitate structural grade metal plating for enhancement of mechanical performance

Nickel Plated Composite Parts:

Property	Improvement
Flexural Strength	30%
Flexural Modulus	100%
Impact Resistance	540%



Application and photo courtesy of Fineline Prototyping

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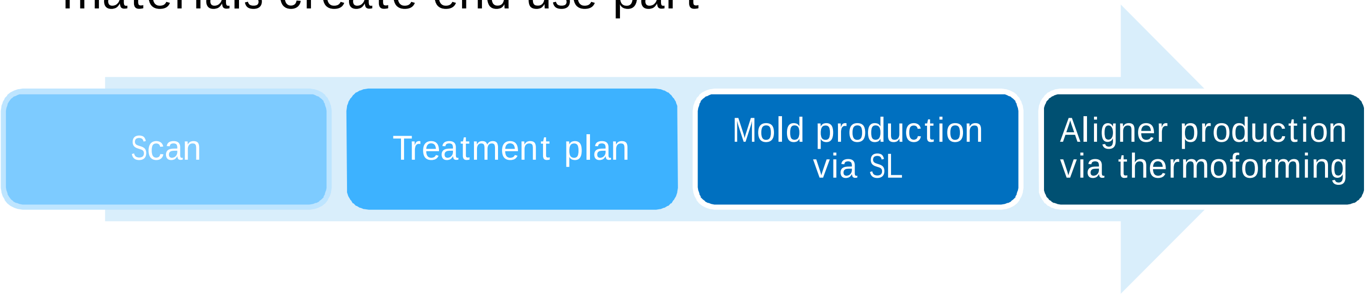
1994 - 2004: SL enables new business models

Dental Aligner Case

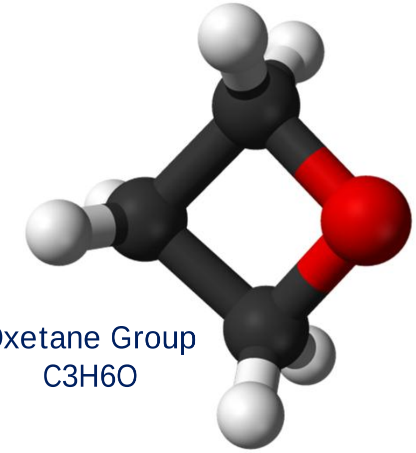
- StudyStereolithography: break-out enabler for the “disruptive” use
  of customized retainers to shape alignment
- Manufacturers adapt /optimize the SL process based on the limited
  geometry variations: speed and low cost is key driver to produce
  custom one-off “tooling”
- Well established thermoforming process and materials create end use part



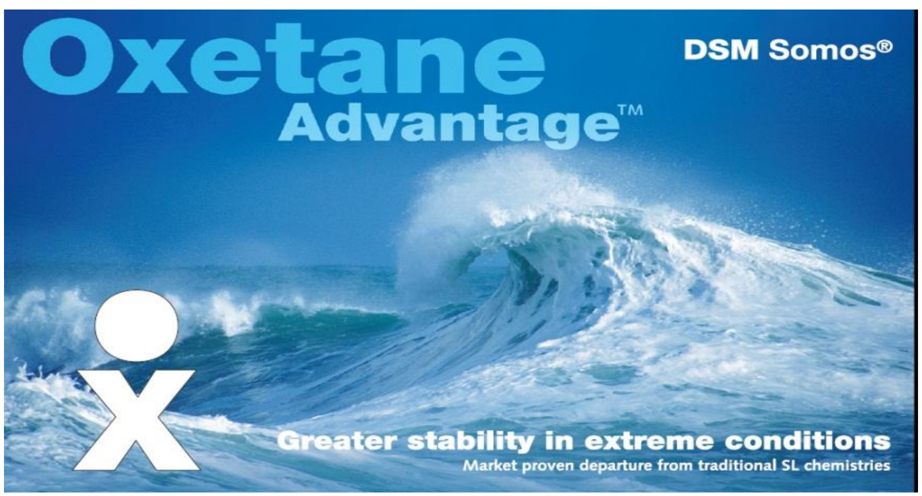
The Diversification Years: 2004 to 2014

Oxetane chemistry widens formulation window

- Typically lower formulation viscosity
- Formulations with excellent moisture resistance
- Higher temperature resistance possible
- Formulations with properties “Tunable” by cure parameters possible



Oxetane Group
C_3H_6O



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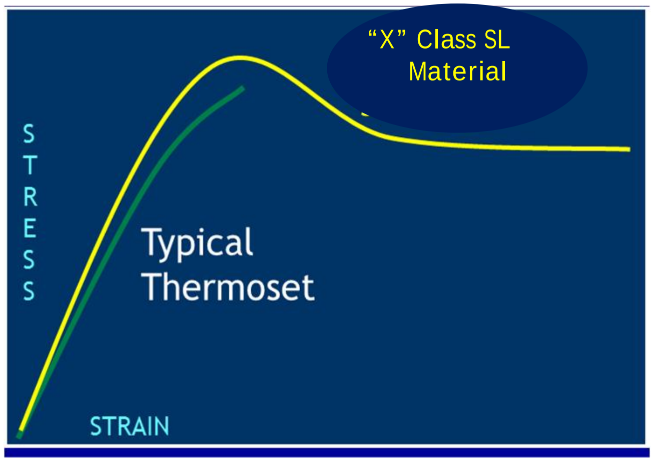
2004 - 2014: Toward engineering thermoplastics

- Goal of SL formulators: *Match the performance of engineering thermoplastics using thermosetting photopolymers*

- "X" class represents formulation versatility possible with SL: proprietary combinations of additives, fillers and hybrid chemistry



		Typical Mechanical Properties		
		PP Like SL	ABS Like SL	"X" Class
Tensile Modulus	MPa	1340	2,700	2400
Tensile elongation	%	20.00	9	20
Izod Impact, Notched	J/m	50	20	66
		TOUGH	STIFF	TOUGH & STIFF

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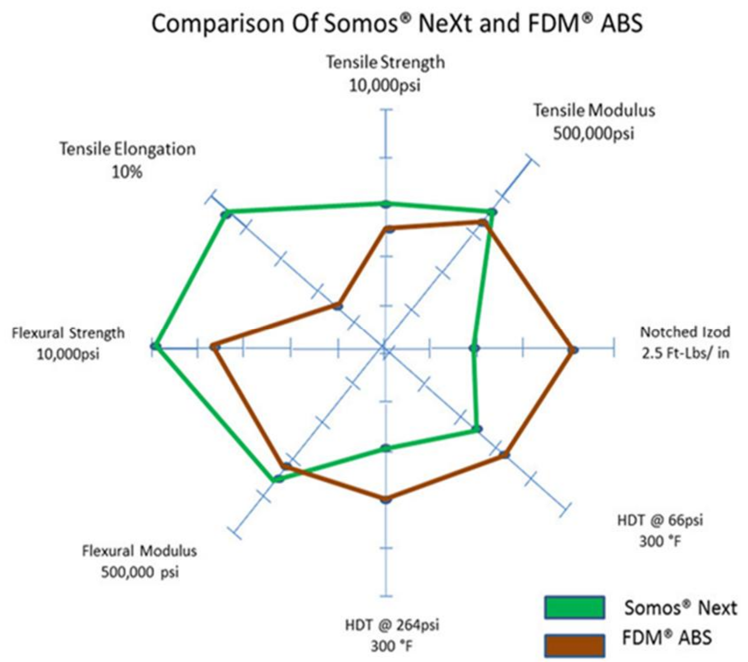
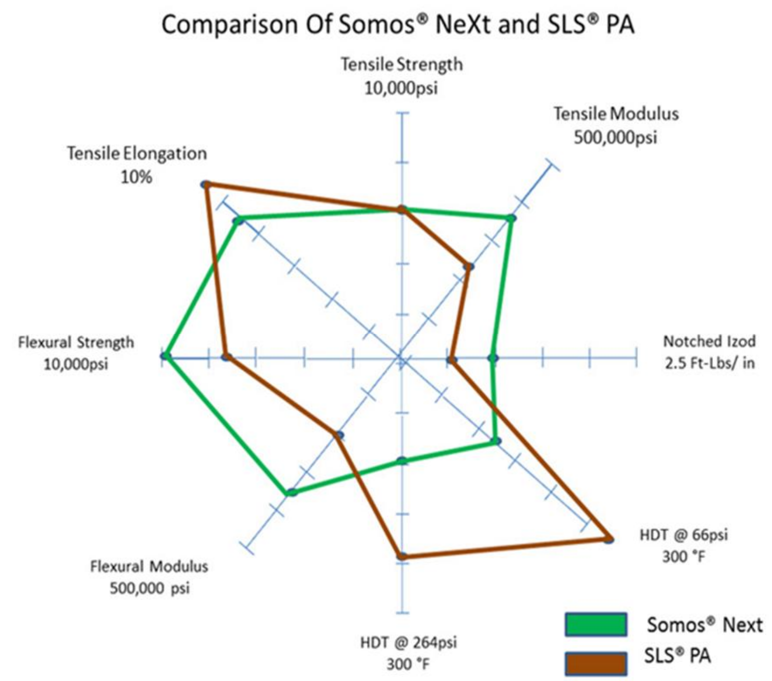
2004 - 2014: "X" Class SL resin competing AM market

- Mechanical performance of "X" class SL material overlaps those of ABS and Nylon-based AM processes
- Advances in material performance expands SL process capability





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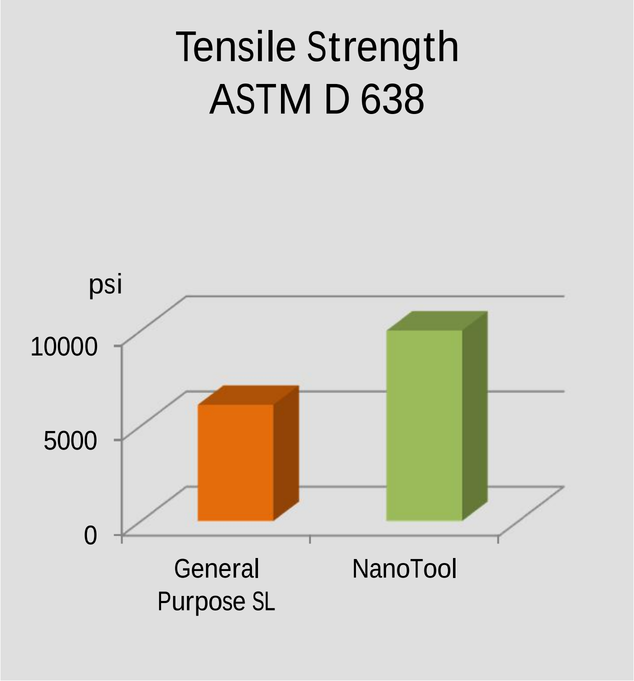
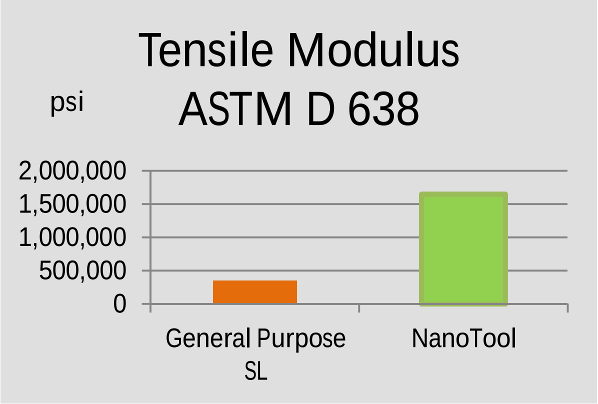
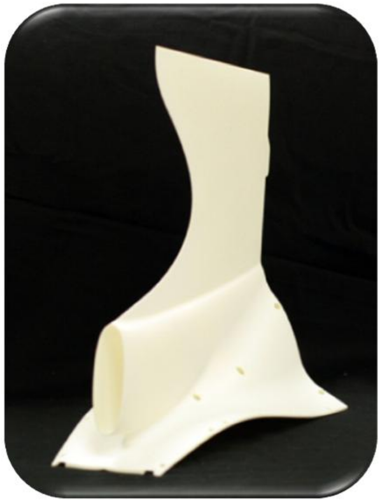
2004 - 2014: Composite SL resin advanced

- Composite SL provides large increases in strength and modulus, while maintaining properties at elevated temperatures compared to general purpose SL materials
- Extensive use in Motor Sports wind tunnel model testing







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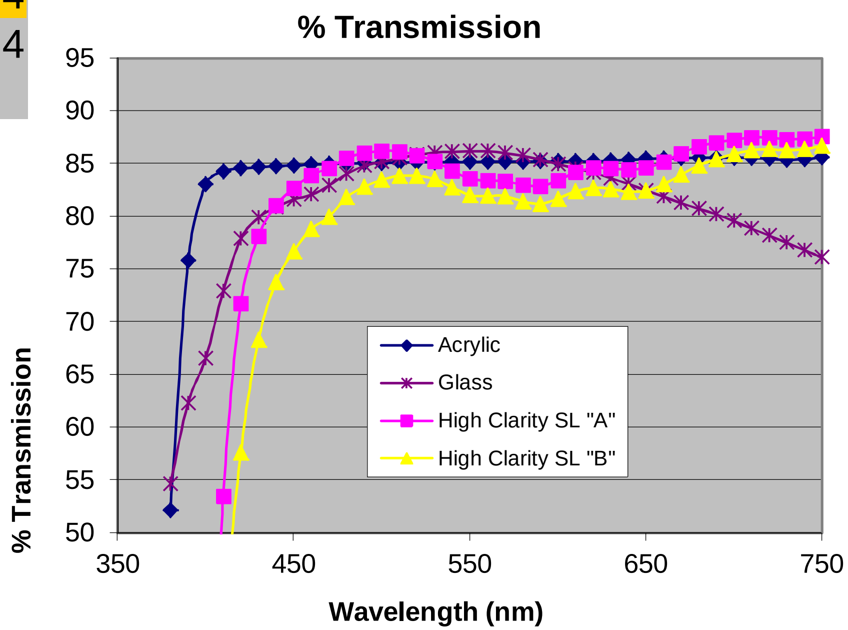
2004 - 2014: High clarity SL resins advanced

Delta E Colorimetry w/Acrylic Standard	
	DE*
Acrylic	0
Glass	2.45
High Clarity SL Resin A	0.596
High Clarity SL Resin B	2.374
Comparative Standard SL Clear Resin	6.514

Improvements in clarity and low color expand utility of SL in consumer goods and automotive prototyping



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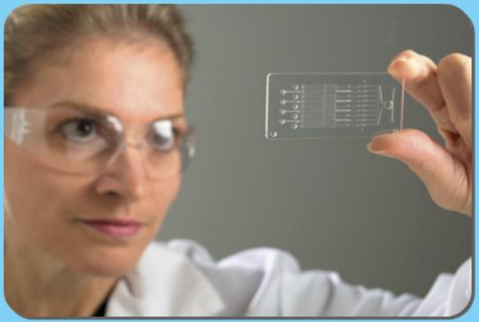
2004 to 2014: New Specialty SL Resins

Specialty SL formulations driven by end use applications

Real Ant !!!



Medical applications

- USP Class VI, ISO 10993-5 (cytotoxicity)
- ISO 10993-10 certified (sensitization)

Antimony Free Material
for special alloy investment casting

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Stereolithography: Looking forward

- Examples of areas for future materials development
  - Temperature resistance
  - Toughness/stiffness combination
  - Mechanical aging characteristics
  - Color stability with UV exposure in use
  - Parameters that affect process speed : imaging and recoating

- Opportunities for leveraging current SL photopolymer expertise
  - SL systems based on even longer wavelength light
  - DLP technologies

- SL equipment and SL applications ......

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We're dedicated to advancing AM

DSM's Somos® materials build on a foundation at the roots of Stereolithography development…

Somos® SL machine, 1992

Our early team in 1989
— Courtesy from Ed Murphy

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…..And look forward to a future of innovation in AM photopolymer material development

Our current R&D team in 2013

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