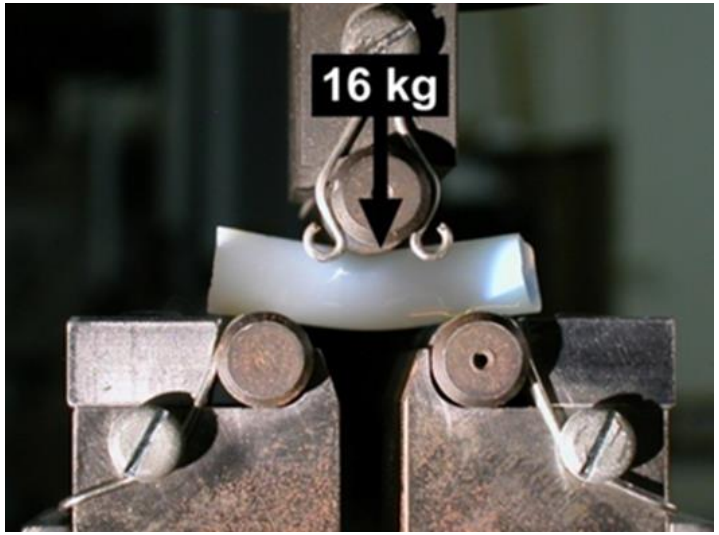
Utilization of Continuous, Low Power, Visible laser in the 3D printing of Strong and Ultra- Light weight Cross-Linked Silica Aerogel







Dr. Khaled Saoud

Associate Professor of Physics

Liberal Art and Sciences Program

Virginia Commonwealth University-Qatar

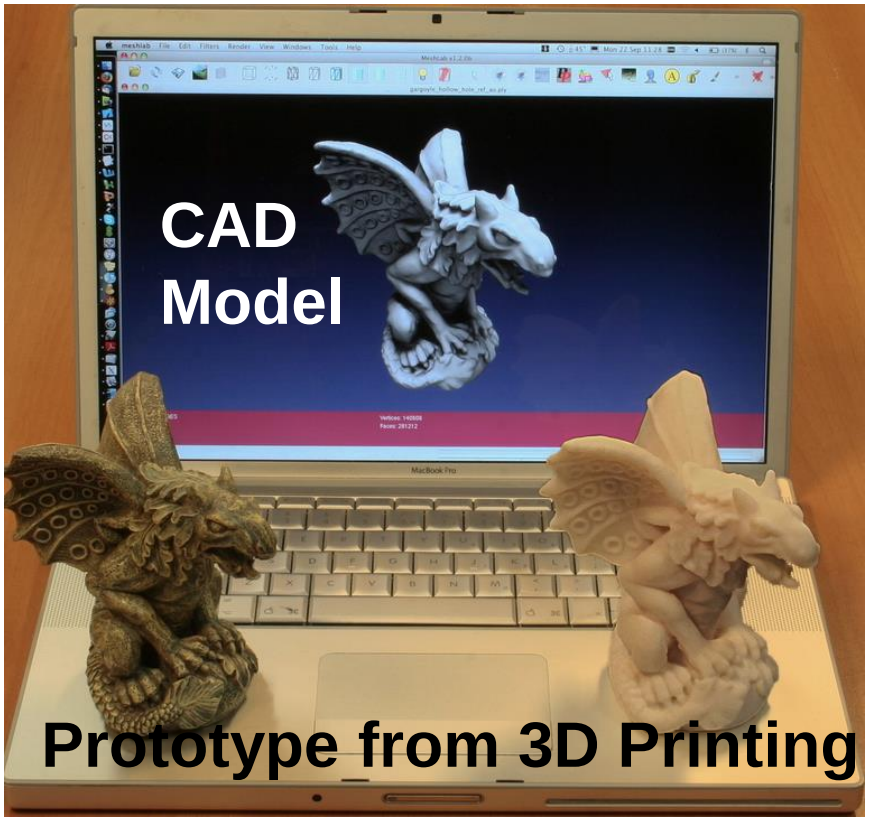
4th International Conference on Photonics and Laser Technology, Berlin, Germany 2016

Outline

- Background
- 3D printing recent advances and challenges
- Types of lasers used in 3D printing
- Aerogel Properties and Aerogel Limitations
- Recent Advances in Aerogel Synthesis and Processing
  - Reducing the Processing time
  - Increasing Mechanical strength of Aerogel (Custom shapes)
  - 3D printing of Aerogel by instantaneous visible laser induces gelation
  - Work in Progress
- Conclusions

What is 3D Printing ?

3D Printing refers to a relatively new class of manufacturing methods which quickly produce three dimensional physical prototypes or solid objects from a digital file.







(Also known as *rapid prototyping*, *layered manufacturing* or *additive manufacturing*)

Brief History of the 3D Printing



- **1976**, The Concept of 3D printing can be traced back to the invention
- of the inkjet printer.
- **1984**, **THE BIRTH OF 3D PRINTING**, the invention of stereolithography, a printing process that enables a tangible 3D object to be created from digital data by **Charles Hull** (the co-founder of 3D Systems).

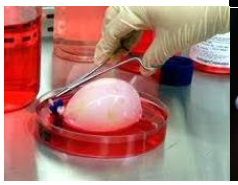
1990s

- **1992**, **BUILDING PARTS, LAYER BY LAYER, The first SLA** (stereolithographic apparatus) machine is produced by 3D Systems.



- **1999,** ENGINEERED ORGANS BRING NEW ADVANCES TO MEDICINE

  The first lab-grown organ is implanted in humans





2000s

- **2002, 3D PRINTED FUNCTIONAL KIDNEY,** that is able to filter blood and produce diluted urine in an animal.
- **2006**, **THE INVENTION OF SLS (selective laser sintering) machine LEADS TO MASS CUSTOMIZATION IN MANUFACTURING**, this machine uses a laser to fuse materials into 3D products.
- 2009, **DIY KITS FOR 3D PRINTERS ENTER THE MARKET**, MakerBot Industries start selling hardware for 3D printers that allow buyers to make their own 3D printers and products. **Dr. Gabor Forgacs's** technology, uses a **3D bioprinter to print first blood vessel**.





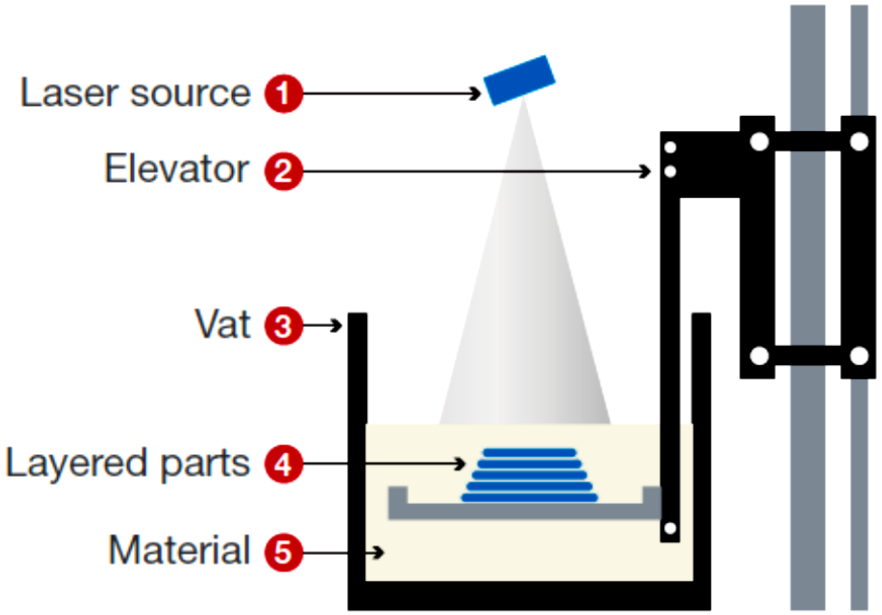
2010s

- **2010**, WORLD'S FIRST 3D-PRINTEDROBOTIC AIRCRAFT
- **2011**, WORLD'S FIRST 3D-PRINTED CAR
- **2011**, 3D PRINTING IN GOLD AND SILVER
- **2012, 3D-PRINTED PROSTHETIC JAW IS IMPLANTED**





HOW 3D PRINTING WORKS



1 A laser source sends a laser beam to solidify the material.

2 The elevator raises and lowers the platform to help lay the layers.

3 The vat contains the material used to create the 3D object.

4 The 3D object is created as parts are layered on top of each other.

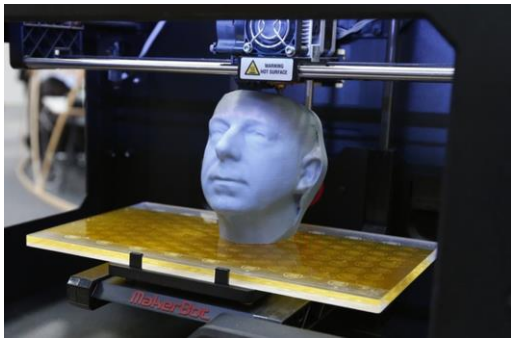
5 Advanced 3D printers use one or more materials, including plastic, resin, titanium, polymers and even gold and silver.

The Birth Of 3D Printing – 3D Systems Corporation



Types of 3D printing technology

- SLS (Selective Laser Sintering)
- FDM (Fused Deposition Modeling)
- SLA (Stereolithography)
- DLP (Digital Light Processing)



Lasers and 3D printing

SLS (Selective Laser Sintering)

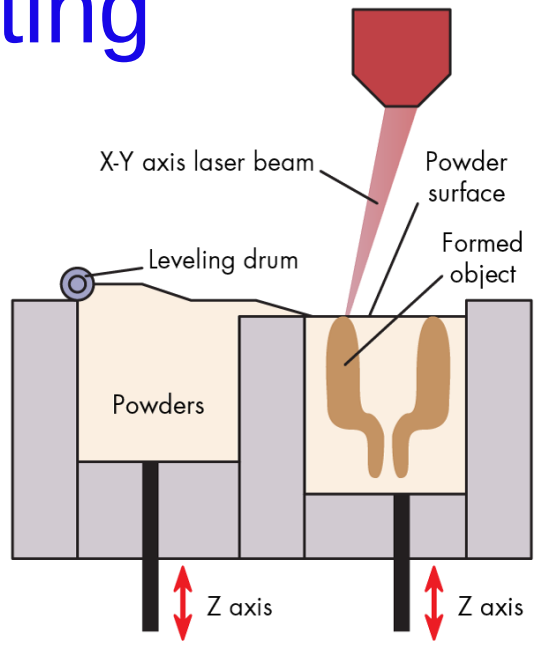
Material:

- Powdered plastics (nylon), metals (steel, titanium, tungsten), ceramics (silicon carbide) and fiber-reinforced

Laser:

- Carbon Dioxide Laser (400nm to 10um wavelength) at (40 mW) power

SLS



SLA (Stereolithography)

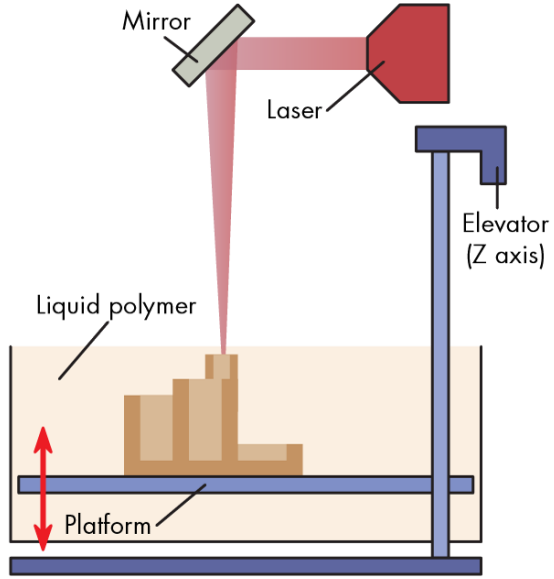
Material:

Photopolymer resin

Type of Laser:

- Ultraviolet (UV) Laser (310 - 355 nm) with 40 mW for HeCd lasers to 600 mW for Argon Ion lasers.

SLA



http://machinedesign.com/3d-printing/what-s-difference-between-stereolithography-and-selective-laser-sintering

Recent Advances in 3D Printing

- 2015, Researchers at and Massachusetts Institute of Technology (MIT) have developed ultralight 3D printing materials.
- 2015, Researchers at VCU Qatar and VCU Richmond developed a new Rapid fabrication technique to 3D print ultra-light and Mechanically strong Cross-Linked silica Aerogel structures using low power visible lasers.
- 2016, Scientists at Lawrence Livermore National Laboratory and UC Santa Cruz have successfully 3D-printed supercapacitors using an ultra-lightweight Graphene aerogel
- 2016, Lawrence Livermore National Laboratory (LLNL) engineers ultra-lightweight and flexible 3D-printed metallic materials.

3D Printing Challenges and Limitations

- Resolution: Stereolithography resolution is several millimeters and layer thicknesses above 1 μm. There is a need for new process with layer thickness from 50 to 150 μm (3D multiphoton Laser lithography- Nanoscribe).

- Materials: Strength and density, two material properties of central relevance for 3D printing. There is a need for Ultra-Light and Mechanically strong Material.

- Cost: Expensive high power lasers , Material cost and Processing time (UV-Curing) are driving the cost of 3D printing. There is a need for one-pot rapid fabrication , cost-effective and upscalable process that utilizes cheap low power Visible lasers with no UV-Curing step.

Nanotechnology Leeds to Revelation in Materials and Processing

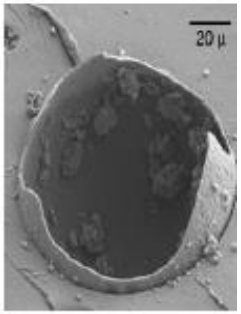

concrete


steel


insulation


glass


drywall



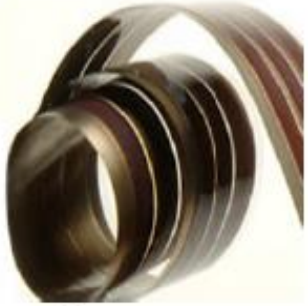
plastic


fabrics
& carpet


energy
& hvac


lighting


air & water
filtration

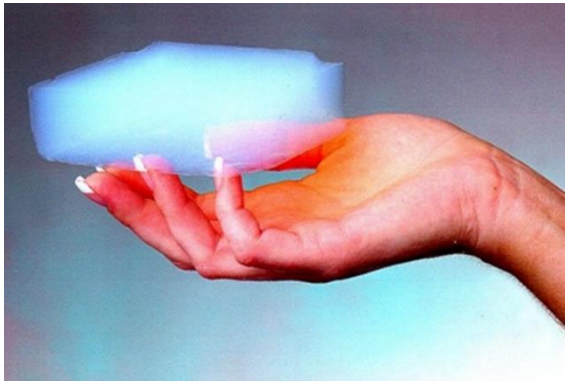

electronics

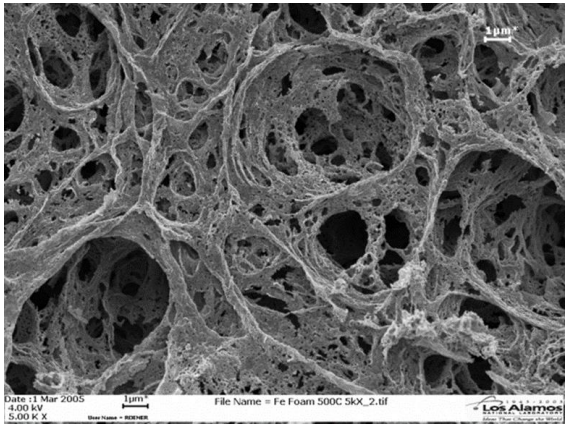

coatings
& paints

Nanotechnology enable sustainable communities by conserving resources, providing new ways to generate energy & potable water, and recycling waste

Aerogels (3D printing Dream Material)

Silica aerogels are unique, Highly porous materials consisting of 90% air and less than 10% solid silica in the form of a highly cross-linked network structure.

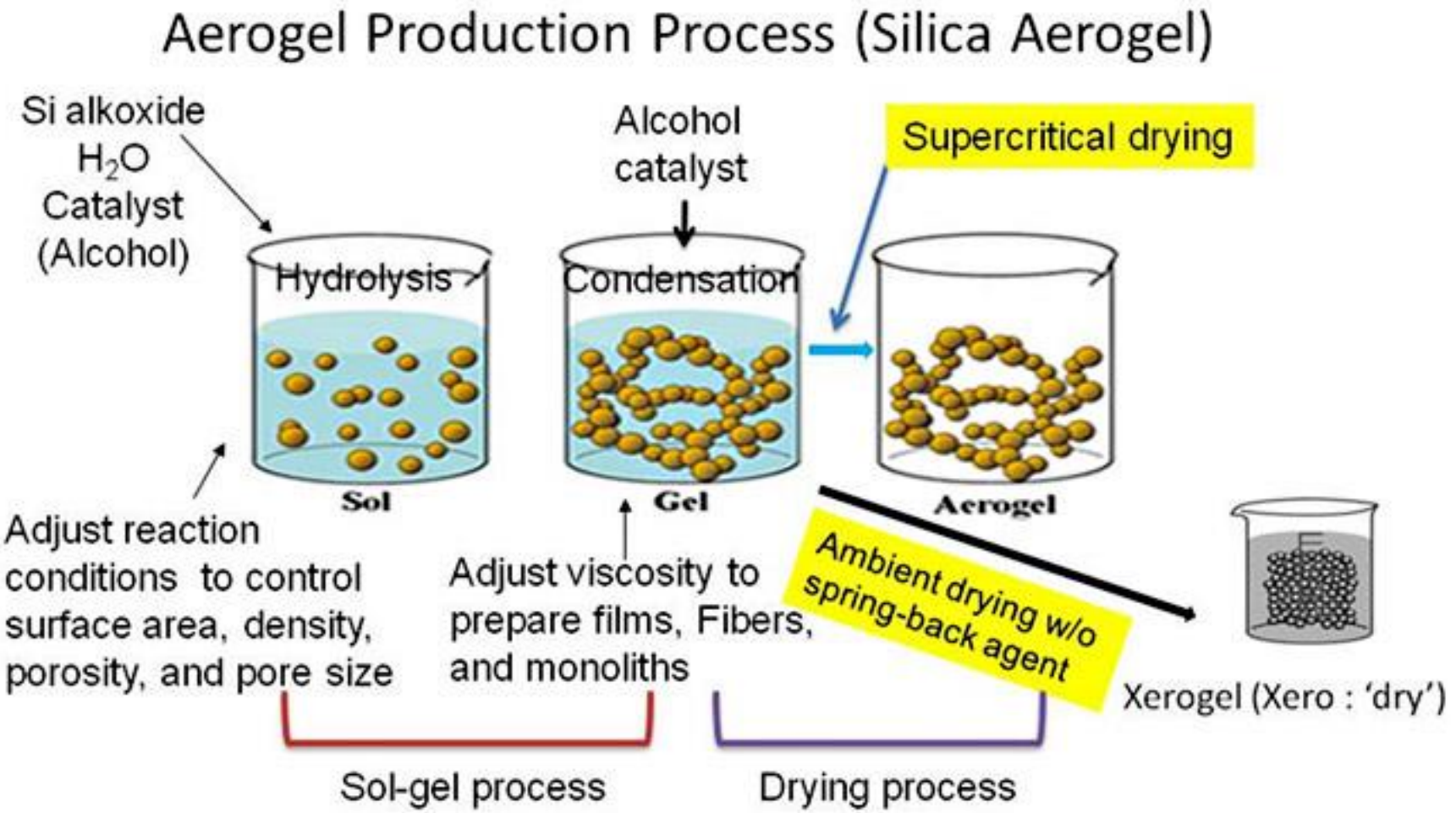




- Created by Steven Kistler in 1931.
- It consists of lightweight silica solids
- aerogel is often called a "frozen smoke";
- Aerogel is the lightest Solid (0.6 g/cm^3) an incredible insulator.
- surface area of between 250 and 3000m^2 per gram
- Aerogel has high Compressive Specific Strength 400000-450000(Nm/kg)
- Best insulating solid in the world
- Extremely flexible: blankets, beads, sheets

Aerogel holds several Guinness records for the World's lowest density solid and the best insulator of any known solid material.

Aerogel synthesis



Aerogel Challenges

- Long processing time: Expensive and VERY long and expensive production process-days/weeks due to multiple solvent exchanges.
- Limited sizes < 10 mm
- Limited Mechanical Strength Has been overcome by cross-linking with a polymer without overly compromising surface area and porosity
- Resulting composites show Young's moduli on the order of a few tens of MPa
- We have showed that modulus could be increased several times by increasing functionality of the cross-linking monomer

Mechanically Strong Aerogels with Custom Shapes

The goal of our research is:

- Research and develop low-cost approaches for the production of photocrosslinkable aerogels with custom shapes.
- Fabrication of proof-of-the-concept parts and make the fabrication procedure simple, cost-effective and upscalable.

Nation

VCUQ research project gets NPRP grant

TRIBUNE NEWS NETWORK
DOHA

VIRGINIA Commonwealth University in Qatar's (VCUQ) project 'Mechanically Strong Aerogels with Custom Shapes', has been awarded an $881,000 National Priorities Research Programme (NPRP) grant by the Qatar National Research Fund (QNRF).

The three-year project aims to develop cost-effective up-scalable fabrication methodology yielding mechanically robust aerogels with custom shapes.

Aerogels are good thermal insulators because they almost nullify two of the

new thermal insulation materials would reduce energy consumption and provide comfort and protection from fire."

Aerogels are ultra-light, highly porous and highly thermally insulating materials. Because of their unique combination of properties, aerogels are being considered for applications as varied as thermal and sound insulation for the aerospace industry, as absorbents for environmental remediation and as catalyst supports.

However, aerogels are also mechanically fragile and their use has been limited to niche applications such as thermal insulation

It's Disne

TRIBUNE NEWS NETWORK
DOHA

THE curtain for the highly anticipated show, Disney On Ice celebrates 100 Years of Magic, will be raised on Thursday at the Qatar National Convention Centre (QNCC).

After months of preparation, the skaters are ready to dazzle audiences as they prepare to take boys and girls, as well as mums and dads, on an enchanting journey through their favourite Disney stories, both classic and new.

Produced by Feld Entertainment, Disney On Ice celebrates 100 Years of Magic brings together an international team of award-winning skaters, well-loved songs, stunning choreography, dazzling sets and beautiful costumes to provide fond Disney memories.

"We are really excited about the start of the shows. The cast and crew have worked extremely hard and many hours have gone into making this mammoth production possible. From the ice rink, to the innovative sets, to iron-on sequins on the costumes, each detail has been fine tuned

GULF TIMES

Qatar › Grant boosts VCUQ thermal insulation materials project

Grant boosts VCUQ thermal insulation materials project

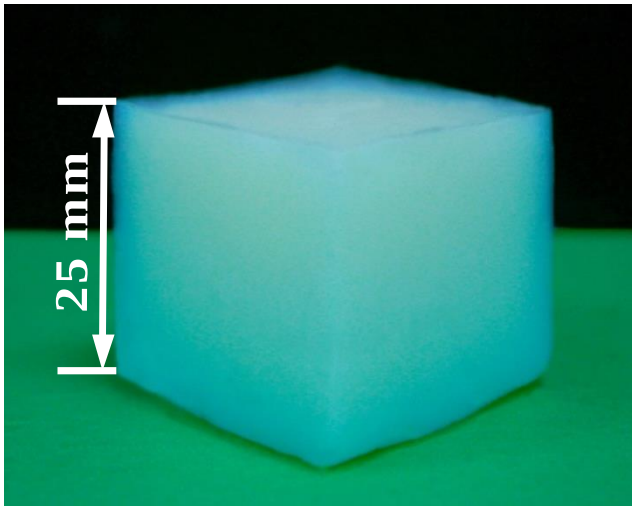


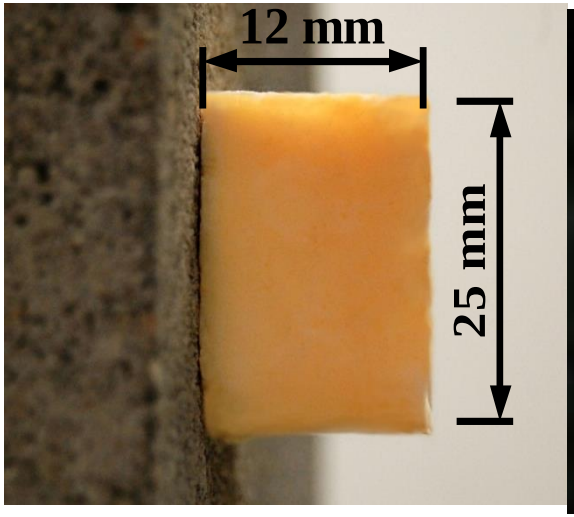
Dr Khaled Saoud and Dr Massimo Bertino.

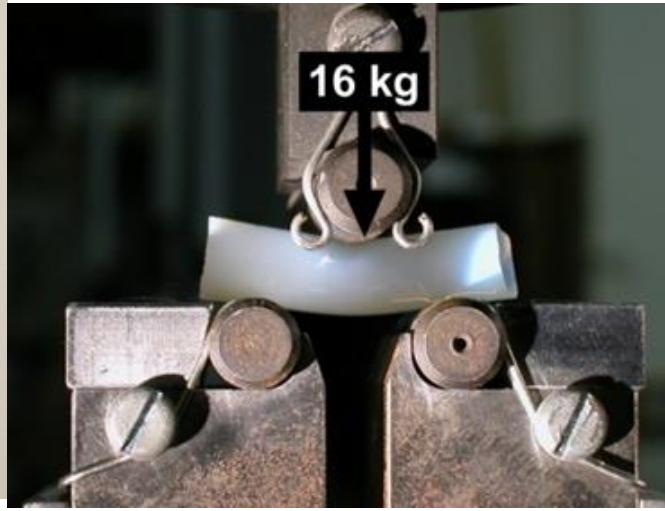
+1 0 Tweet 0 Like 0

Our Solution (Photogelation using LED light)

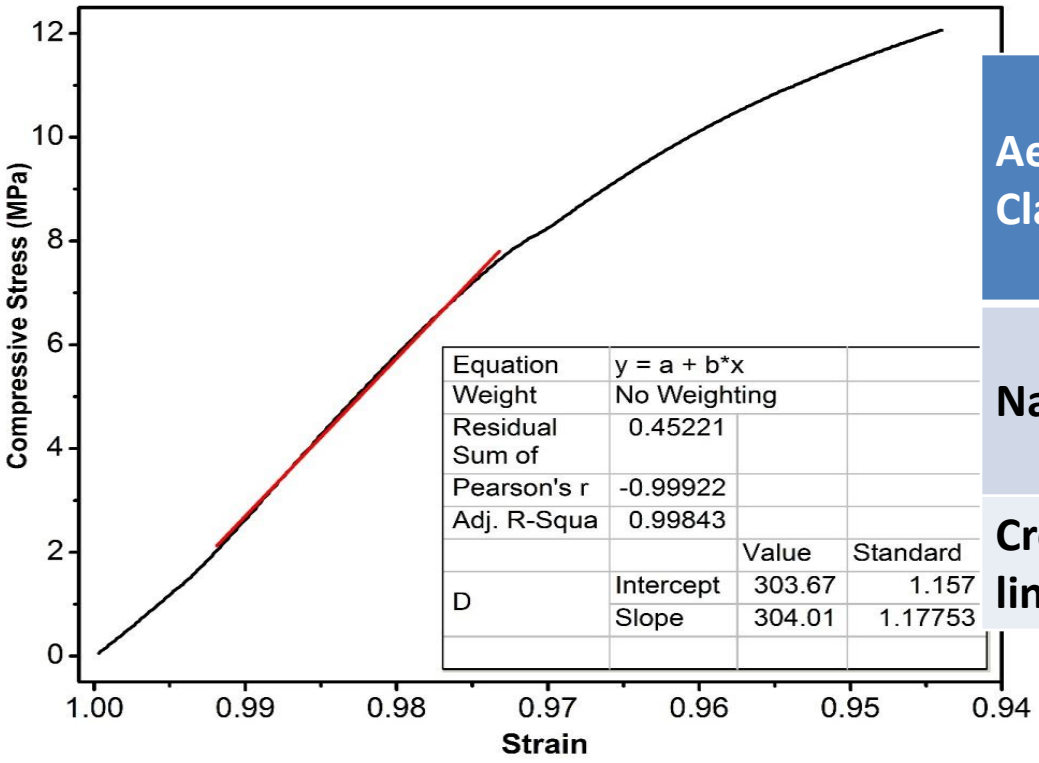
- **Novel formulation**
- Aerogels fabricated in a few hours and now less than 1 minute
- Fabrication time does not depend on the part size
- “Regular” and Cross-linked aerogels are fabricated at the same pace







Physical Properties of Aerogels

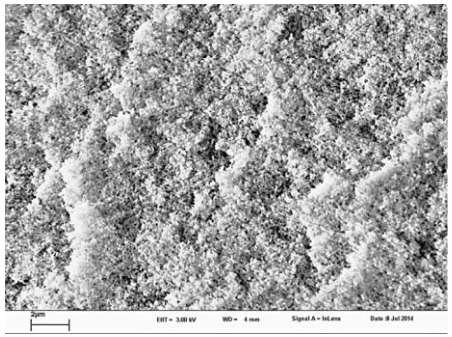


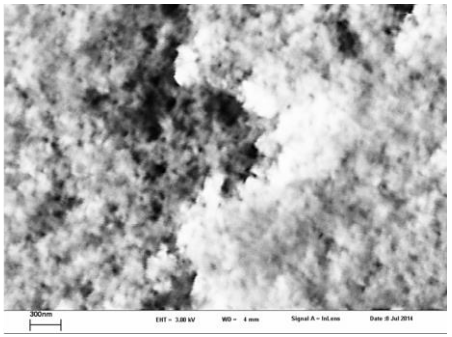
Aerogel Class	BET Surface Area (m^2/g)	Density (g/cm^3)	Modulus (MPa)
Native	**510**	**0.03**	**Not Measureable***
Cross-linked	**350**	**0.82**	**304**

* monolith cracked when contacted by anvil

304*145= 44080 PSI

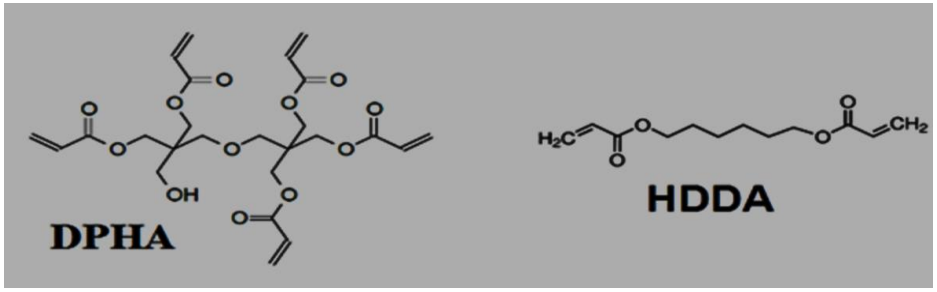
Shortened aerogel fabrication times

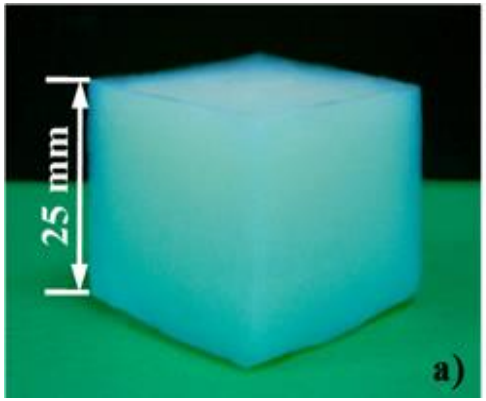


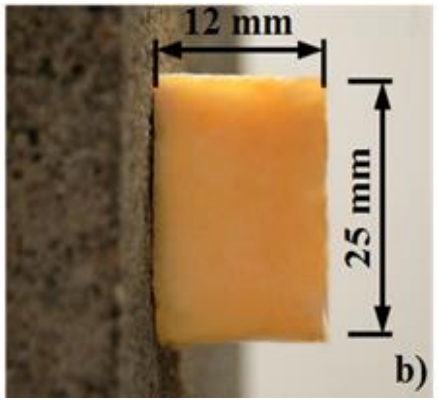


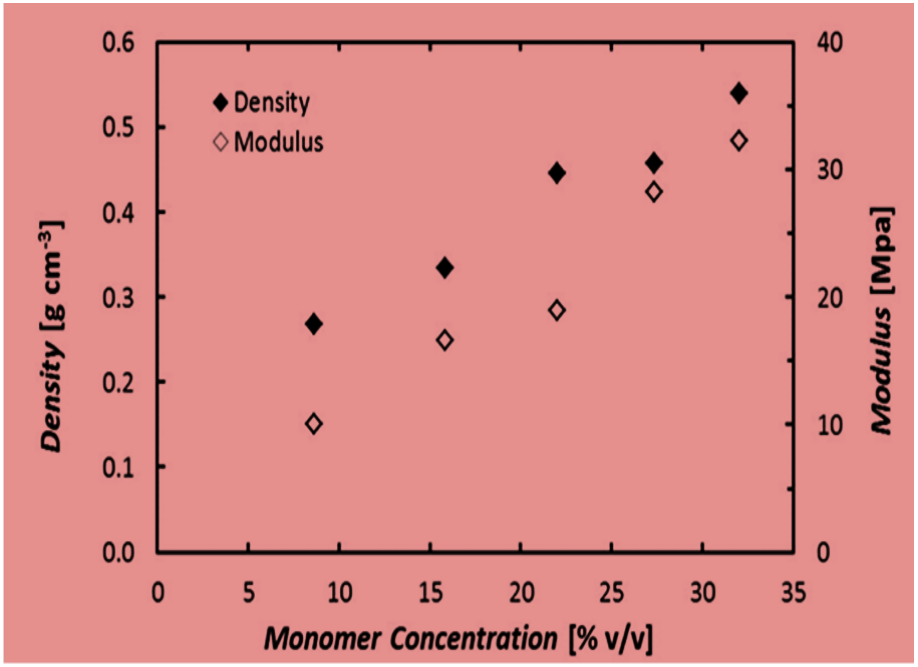
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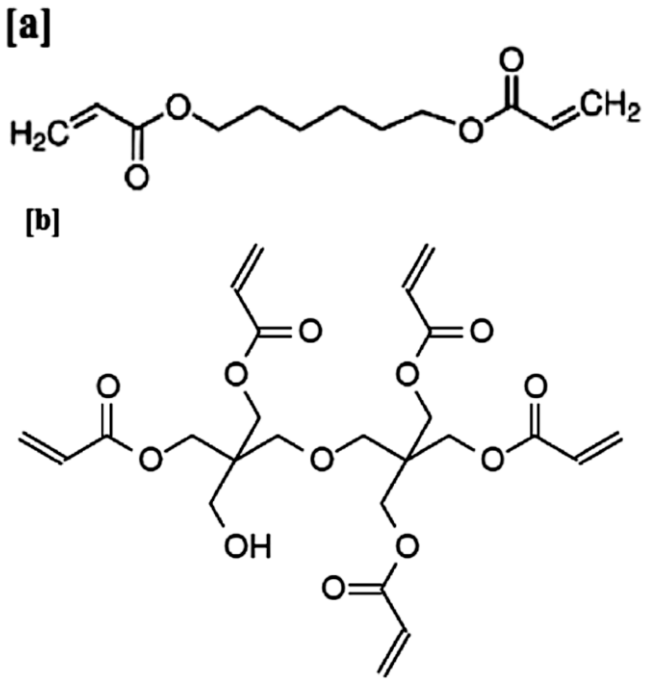




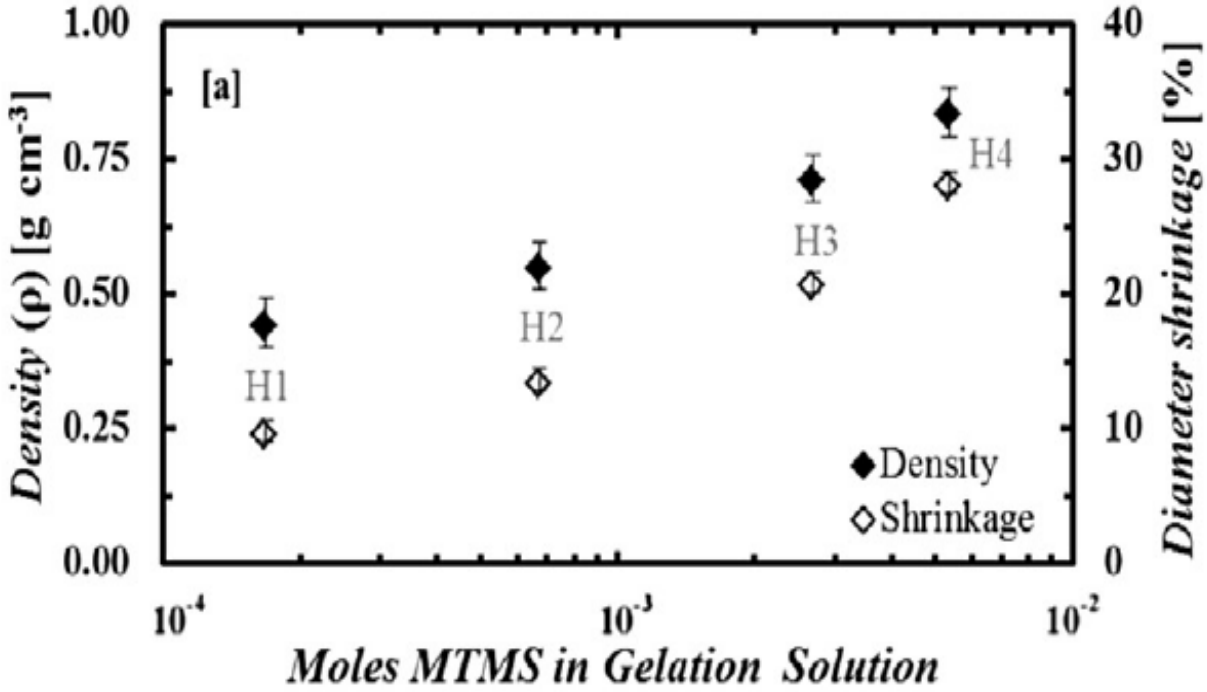


Lauren White, Massimo Bertino, Rola Al-Soubaihi, Shaukat Saeed, Khaled Saoud, Journal of Materials Chemistry A, 2015, 3, 762–772

Dependence of density and linear shrinkage on MTMS Concentration.

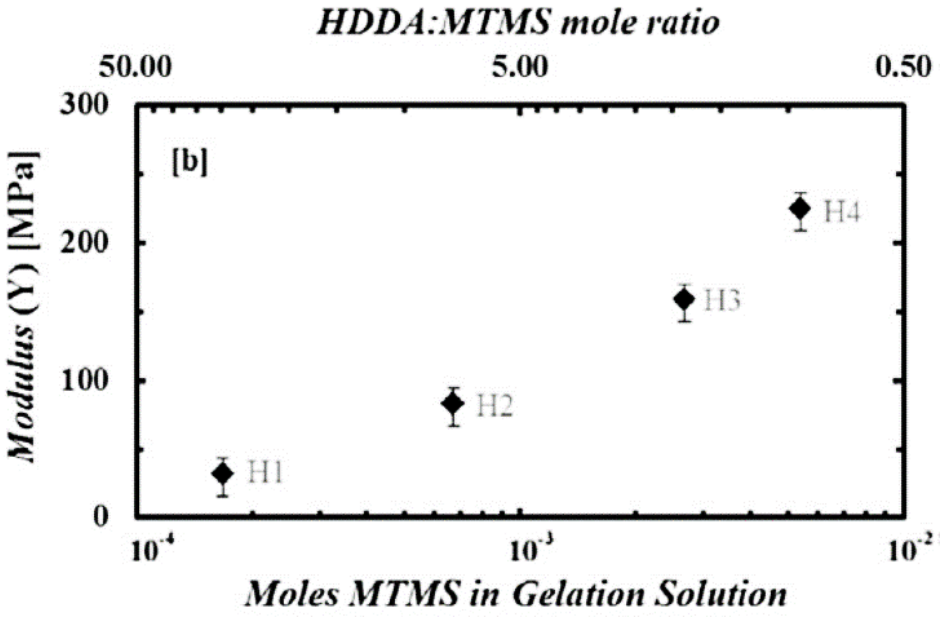


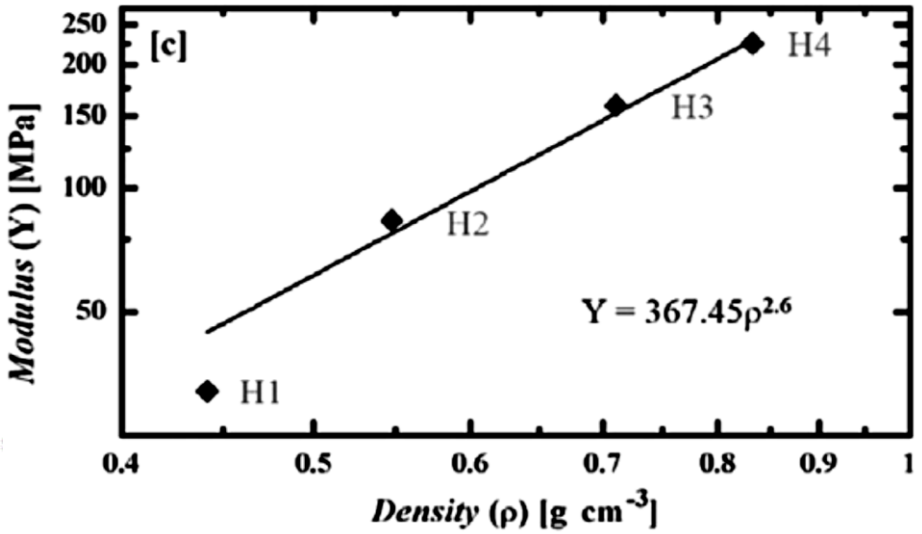
[a] Hexanedioldiacrylate (HDDA),
[b] Acrylated Dipentaerythritol (DPHA)



Lauren White, Massimo Bertino, Shaukat Saeed, Khaled Saoud, Microporous and Mesoporous Materials 217 (2015) 244-252

Dependence of Young's modulus on MTMS concentration

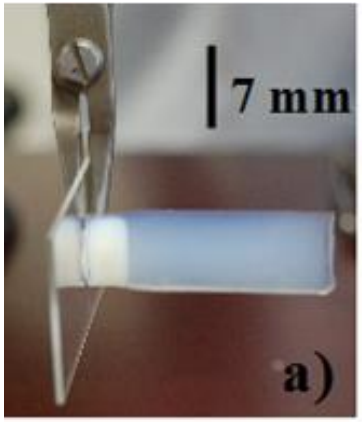


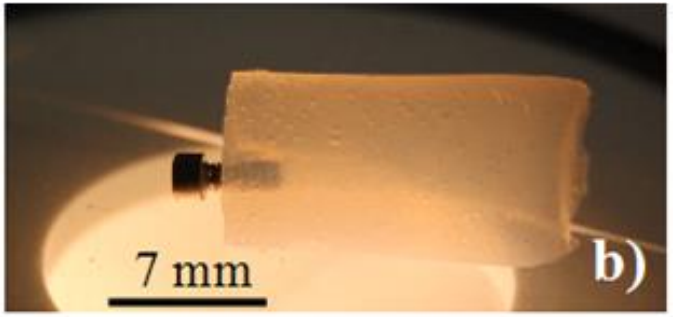


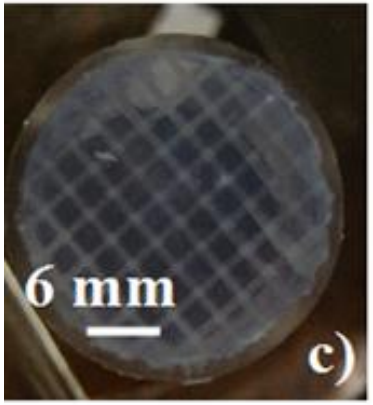
Lauren White, Massimo Bertino, Shaukat Saeed, Khaled Saoud, Microporous and Mesoporous Materials 217 (2015) 244-252

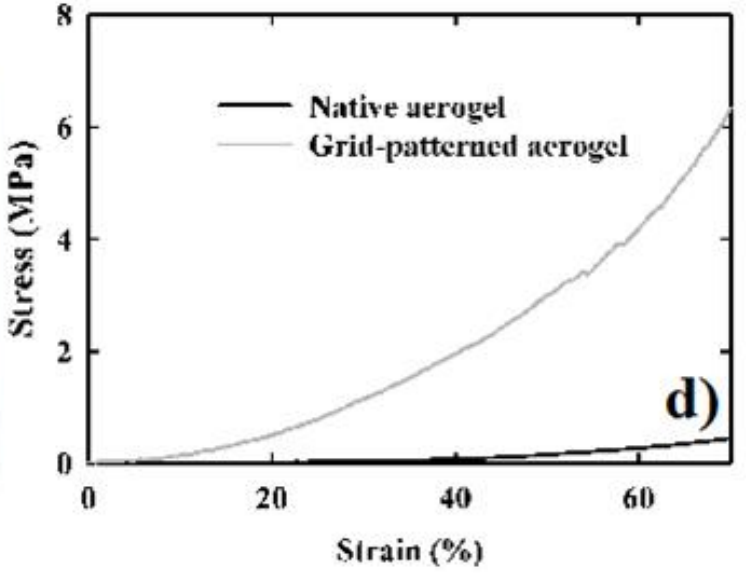
Native Aerogel Monoliths with Selected Areas Reinforced by Photocrosslinking

A. Cross-linked region glued to a glass slide.
B. Fastener screwed into a hole drilled and tapped for a 2-64 thread inside a photocrosslinked region.
C. A square grid honeycomb pattern.
D. Uniaxial compression of a native aerogel and of an aerogel patterned with a square honeycomb grid.

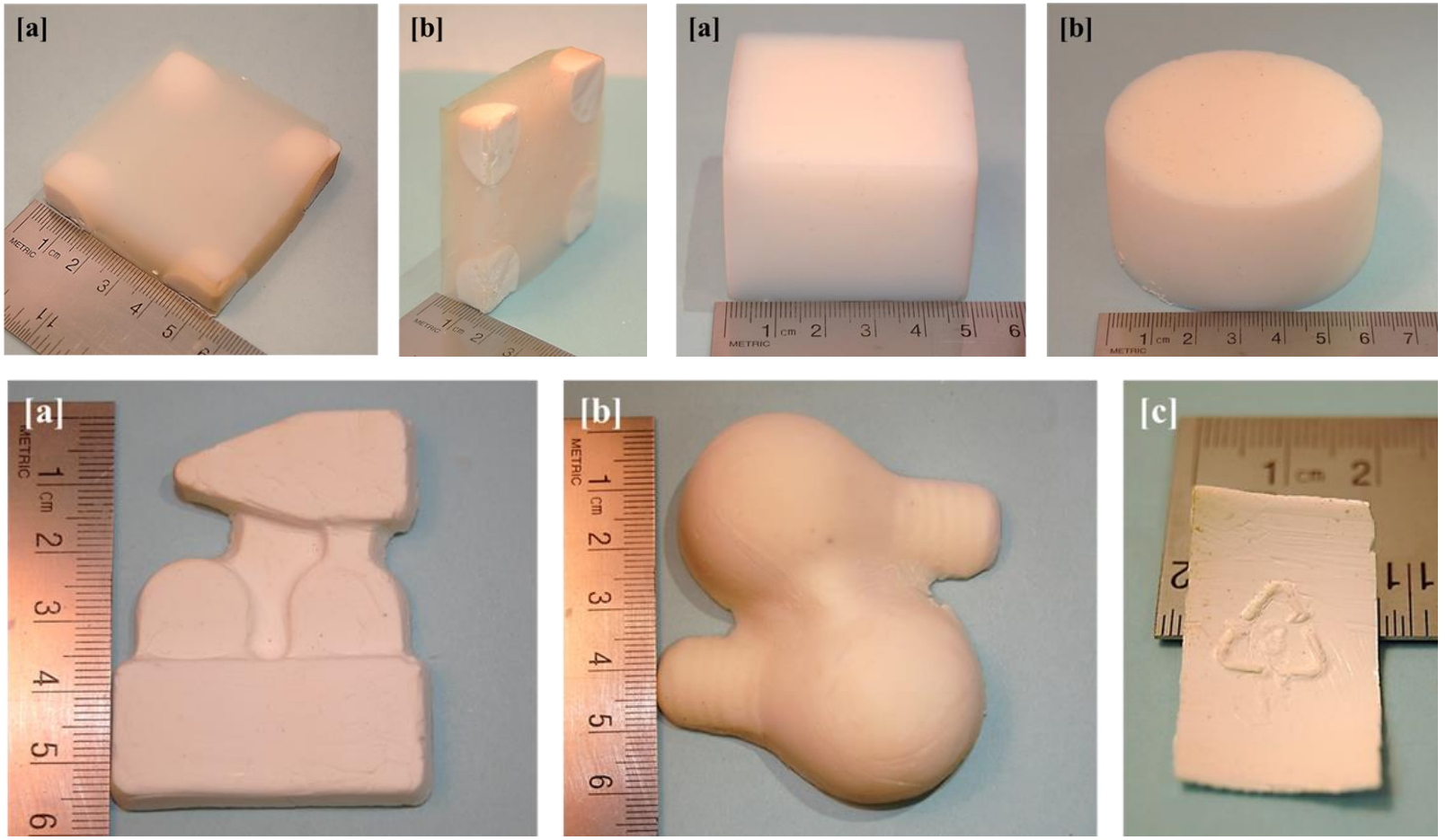








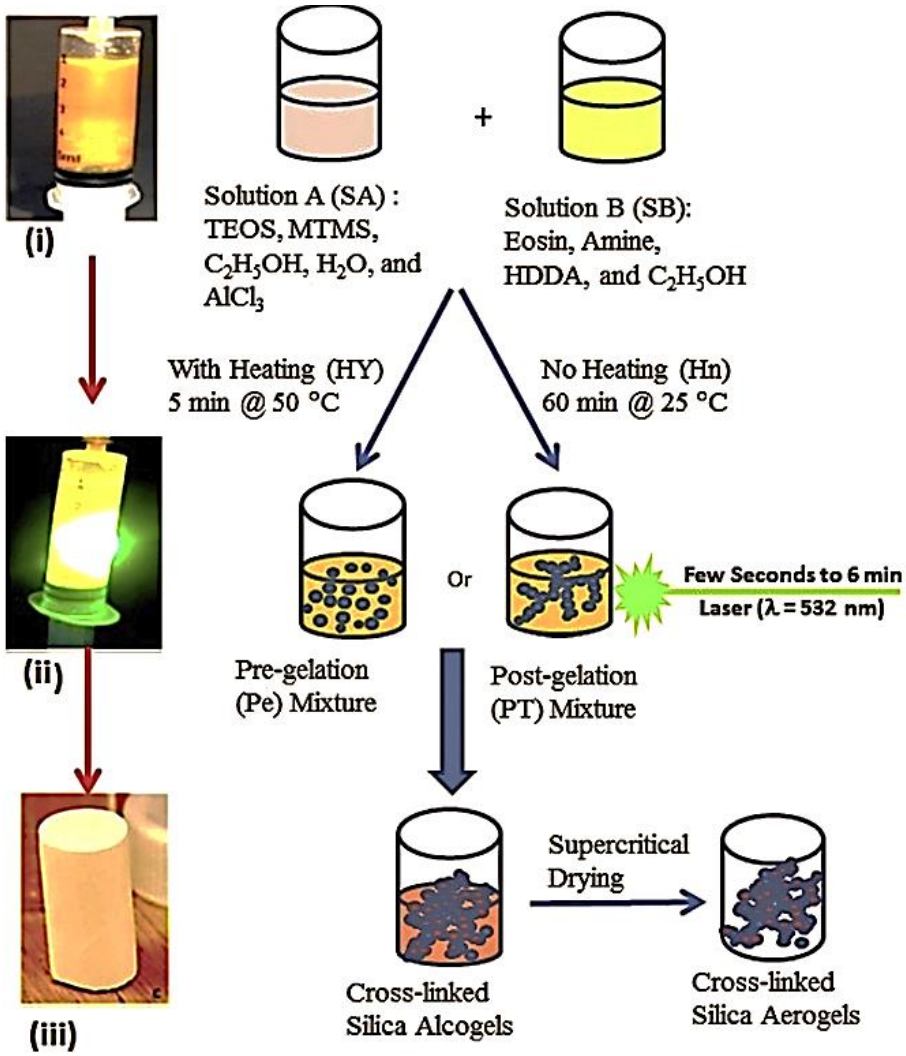
Fabrication of Native Silica, Cross-Linked, and Hybrid Aerogel Monoliths with Custom Geometries



L S White, D R Echard, M F Bertino, X Gao, S Donthula, N Leventis, N Shukla, J Kośny, S Saeed, and K Saoud, Published 11 February 2016 • © 2016 IOP Publishing Ltd
Translational Materials Research, Volume 3, Number 1.

Laser Induced Photogelation Process for Fabricating Cross-Linked Aerogel

In our method, a precursor solution of an alkoxide, a monomer and a visible-light photo-initiator is prepared and illuminated with a high intensity green laser beam that starts free-radical polymerization and triggers gelation.

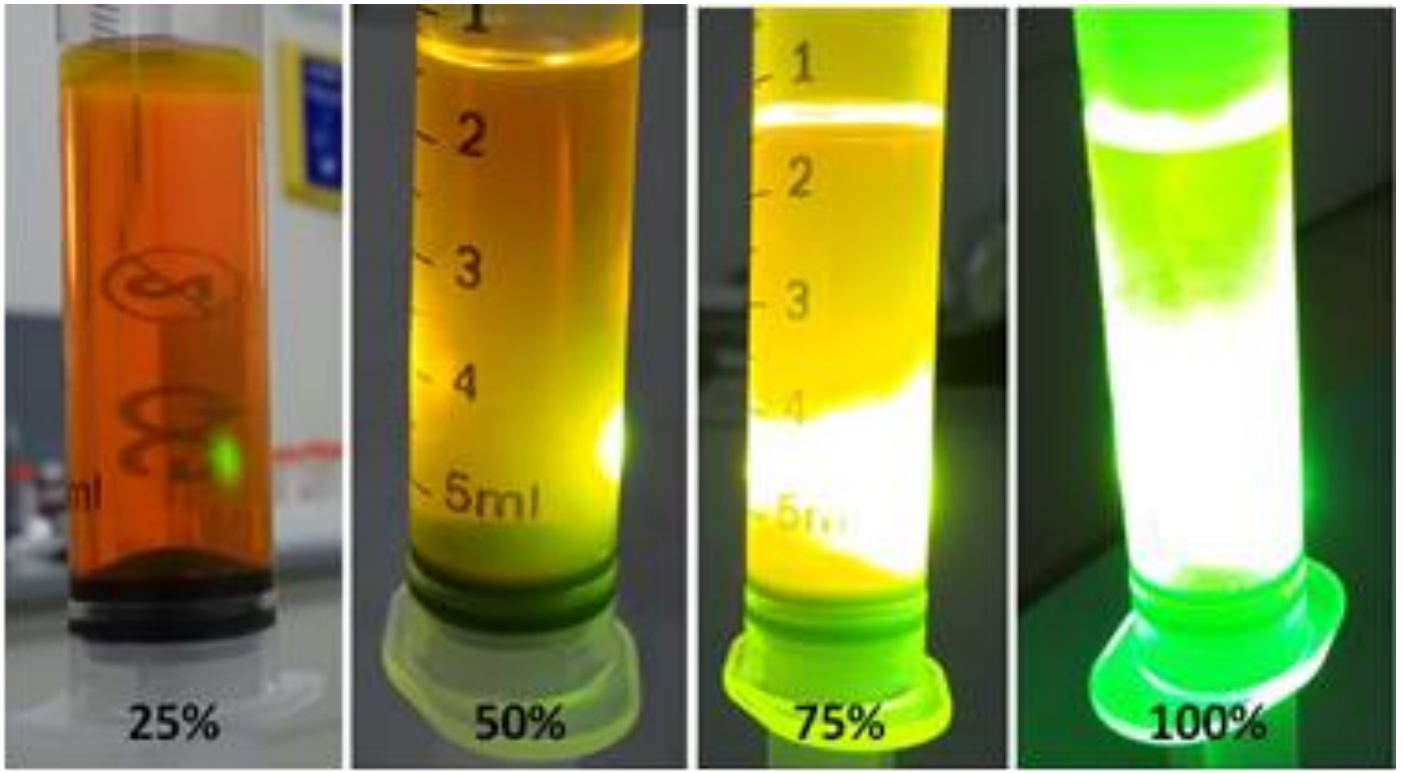


Shaukat Saeed , Rola M. Al Soubaihi , Lauren S. White , Massimo F. Bertino b, Khaled M. Saoud, Microporous and Mesoporous Materials 221 (2016) 245-252

Visible Laser for Aerogel Fabrication

- 2 Watt, continuous wave, diode-pumped solid-state laser emitting light at a wavelength of 532 nm was employed.
- at 75% and 50% of the maximum power of the laser source lead to uniform gelation in few second.
- Eosin Y, which absorbs in the green region of the visible spectrum, was used as the photo-initiator and the tertiary amine acted as co-initiator.
- Upon light absorption, charge is transferred between Eosin Y and the amine, resulting in a reduced radical dye and a radical capable of initiating polymerization. The heat of polymerization triggers instant gelation.
- Typical exposure time ranged from 30 s to 120 s, and the dose in terms of photon bombarded was $1.6*10^{20}$ to $6.4*10^{20}$ photons, when the beam intensity at sample location was 0.16 W/mm^2.

Laser Power study



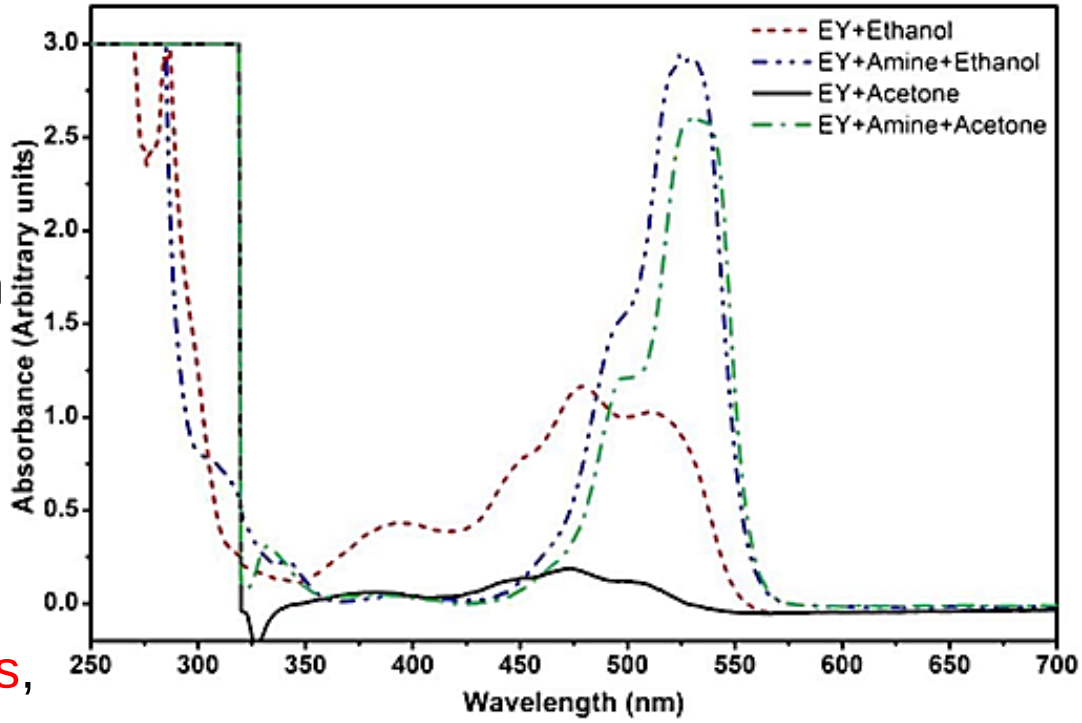
Side-view of the illumination of the samples at different power levels of laser source

Sample	Shrinkage (%)	Density (g/cm^3)	Young's Modulus (MPa)	BET surface area (m^2/g)
$PtHyL_{50}$	12.0	0.59	64.4	154.0
$PtHyL_{75}$	12.8	0.57	78.1	141.7
$PtHyL_{100}$	13.6	0.58	96.7	144.8

- Increasing laser power result in increase of shrinkage, Young's modulus, and a decrease in the surface area

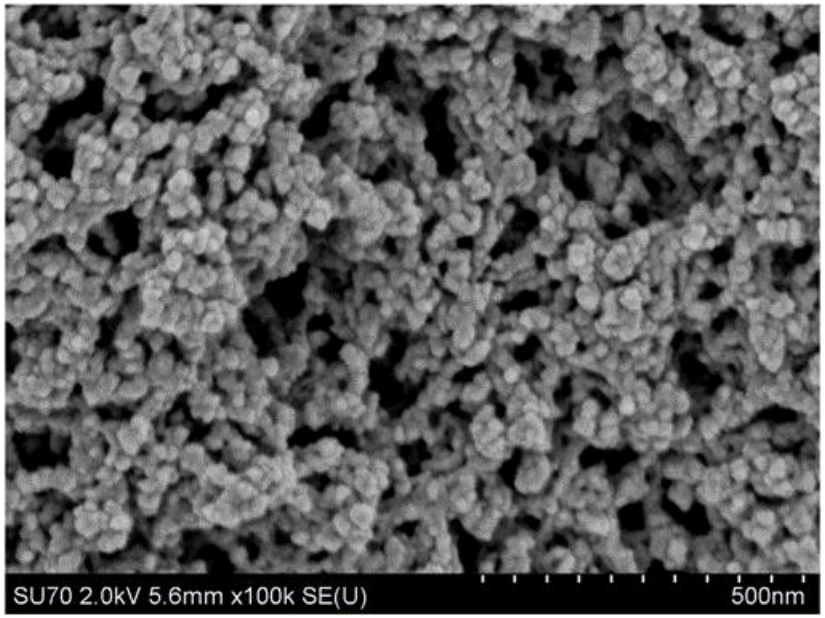
Characterization of The Aerogel Materials Fabricated using Visible Laser Induced Photogelation Method

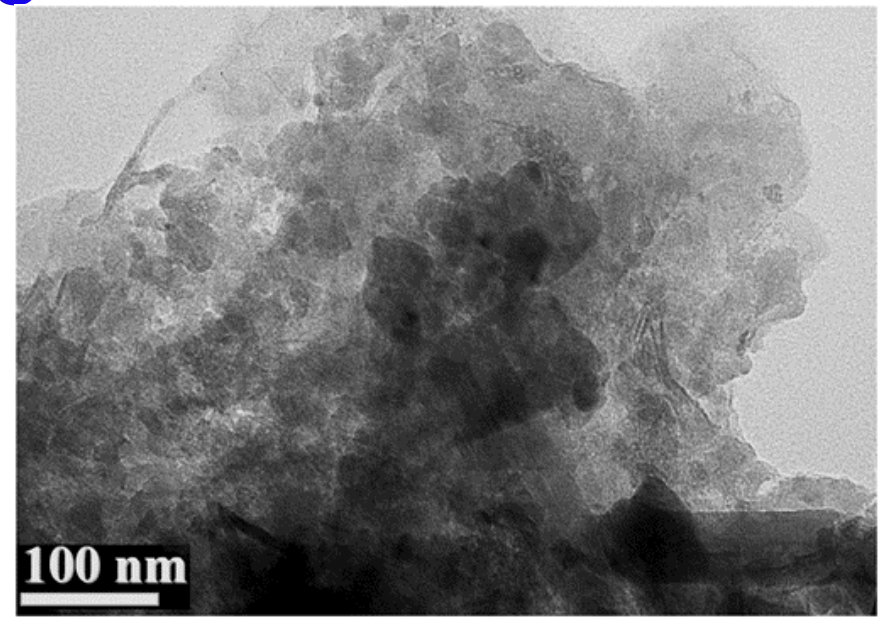
- There is significant enhancement in absorption that has a direct influence on the photo-polymerization leading to instantaneous gelation.
- Eosin Y (EY) solution, played an important role in photo-polymerization and instant gelation.
- There is almost no difference in the magnitude of absorption around 380 nm for both solvents,
- The addition of amine causes a significant increase in the absorption and shift the absorption from 475 nm to 575 nm.



UV-VIS Absorption Spectra of the Monomers, Eosin Y (EY) and Different Solvent

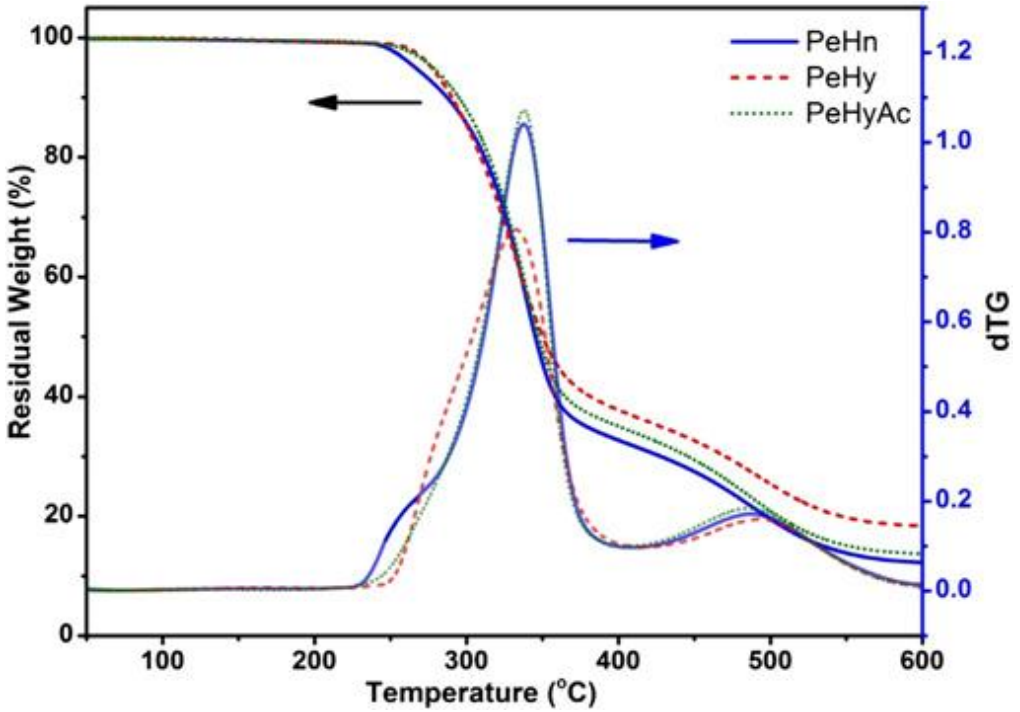
SEM and TEM Morphological Evaluation of the Aerogel Materials.





- The SEM and TEM micrographs clearly show skeletal structure where the particles are coated with the polymer and are interconnected.
- The apparent particle sizes range from 10 nm to 40 nm in all samples.
- Aerogels are mesoporous, with defined interconnected pore structure with average pore size ranges from 17 nm to 29 nm.
- Primary particles could not be observed using SEM because of the polymer cross-linking, as is standard for this class of materials.
- TEM confirms the interconnected structure and shows that the skeletal structure is composed of particles having a diameter ranging from 10 to 30 nm.

TGA and dTG Thermograms of Aerogel Samples



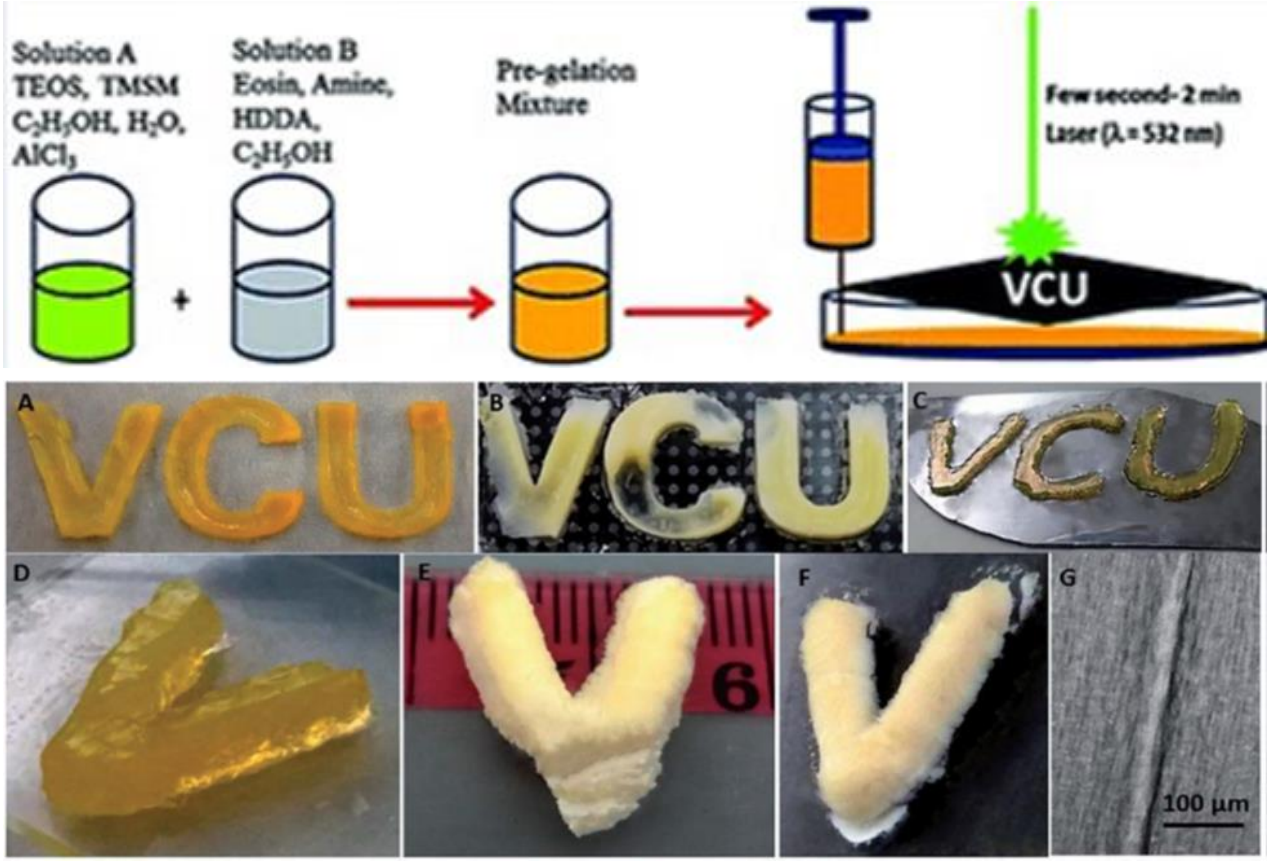
- TGA thermograms shows that all the three samples are fairly stable up to 230 ^{o}C and starts degrading up to 350 ^{o}C.
- The dTG thermograms show that the degradation rate is highest for all samples around 350 ^{o}C.
- the TG and dTG curves that pre-heating had a positive effect in the case of samples prepared in ethanol which show better thermal stability in comparison with samples prepared without pre-heating.

Physical and mechanical properties of aerogel samples.

Sample	Shrinkage (%)	Density (g/cm^3)	Young's Modulus (MPa)	BET surface area (m^2/g)
PeHn	9.6	0.44	31.0	92.6
PeHy	14.4	0.56	88.8	153.8
PtHn	10.4	0.56	81.3	150.8
PtHy	12.8	0.59	98.8	137.8
PeHyAc	21.6	0.80	245.6	78.8
PtHyAc	22.4	0.82	304.0	103.7

- The preheating of the pre and post gelled samples shows enhanced physical properties such as shrinkage, density, Young's modulus, surface area with exception of the increase of Young's modulus and decrease of the surface area and shrinkage of the post gelled sample.
- Using acetone in the processing step increase Young's modulus by order of magnitude and surface area in case of post gelled sample compared to ethanol.

3D Printing of Ultra-Light and mechanically Strong Aerogel on Different Substrates using Low Power Visible Lasers with resolution of 10μm



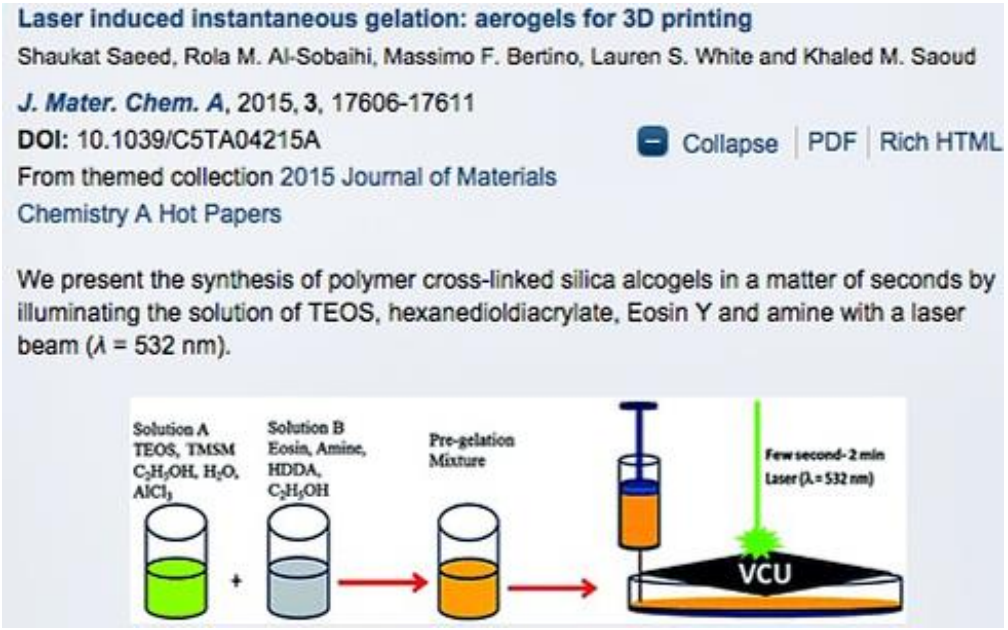
Physical properties: Shrinkage: 10.4% Density: 0.56 g/cm^3 , Modulus: 81.3 Mpa, BET surface area: 155.3 m^2/g

Shaukat Saeed, Rola Al Soubaihi, Massimo Bertino, Lauren White and Khaled Saoud, Journal of Materials Chemistry A, 2015, DOI: 10.1039/c5ta04215a

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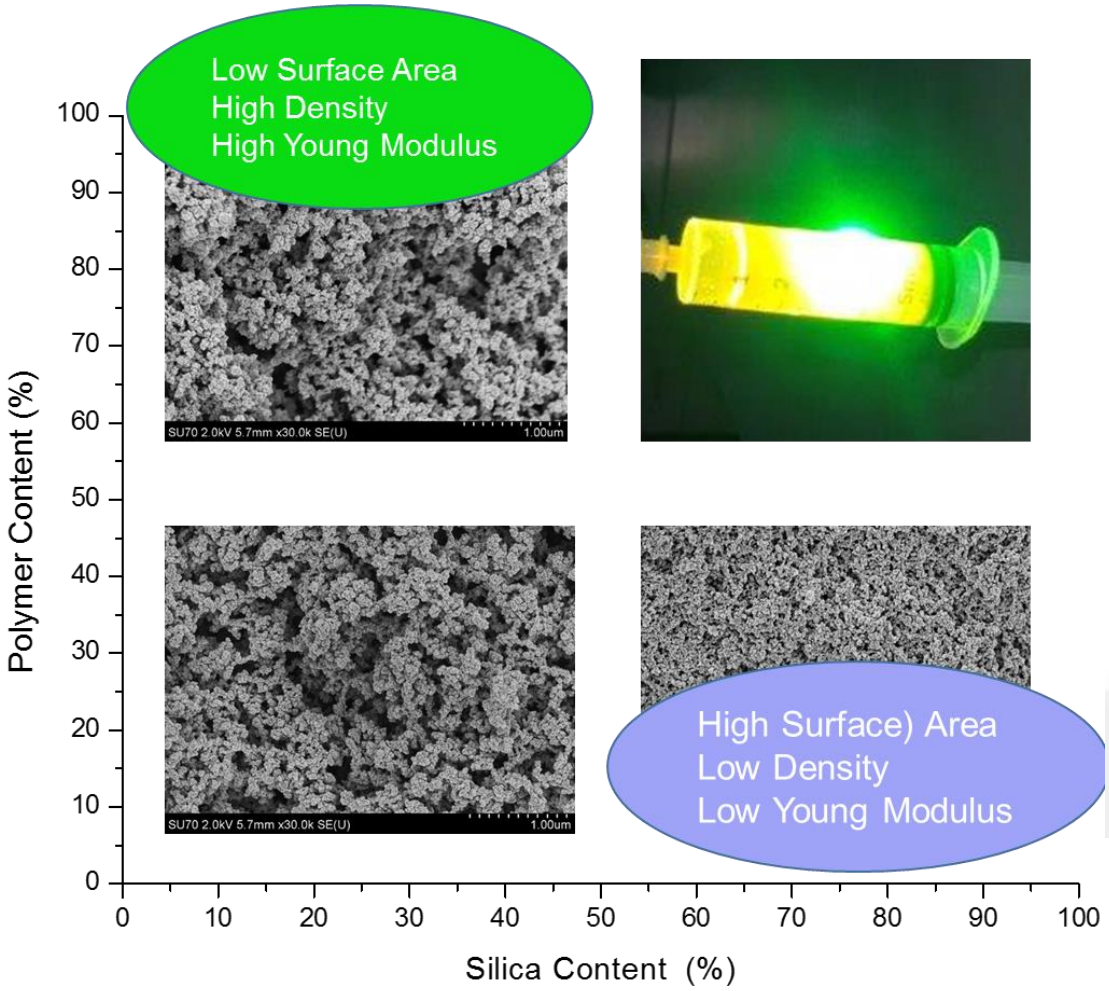
Laser Induced Instantaneous Gelation: Aerogels for 3D Printing





Shaukat Saeed, Rola Al Soubaihi, Massimo Bertino, Lauren White and Khaled Saoud, Journal of Materials Chemistry A, 2015, DOI: 10.1039/c5ta04215a

Work in Progress:
Tuning of the Physical Properties of Visible light 3D Printed Aerogel





Conclusions

- we successfully synthesizes polymer cross-linked silica Aerogel in a matter of seconds by illuminating a precursor solution of an alkoxide, a monomer and a visible-light photo-initiator using a 2 Watt laser beam (532 nm).
- The illumination initiates free-radical polymerization then the heat of polymerization triggers gelation instantly.
- We have successfully 3D print letters on different substrates like laminated paper, a glass slide and a silicon wafer using masking techniques,
- We print a 50 mm thick line on a glass substrate through direct shining of a laser on the liquid mixture without any mask.
- Our results indicate that the instantaneous and simultaneous polymerization and gelation can lead to the fabrication of mechanically strong and ultra-lightweight silica aerogels which offers a new direction for the 3D industry.
- Reducing processing time makes Aerogels cost effective
- We are the first group to utilizes Visible light lasers for instantaneous 3D printing

Acknowledgments

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Thank you
Questions???



