NanoInnovatio Rome
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ISTITUTO ITALIANO
DI TECNOLOGIA

A new approach for the DLP-3D printing of functional materials

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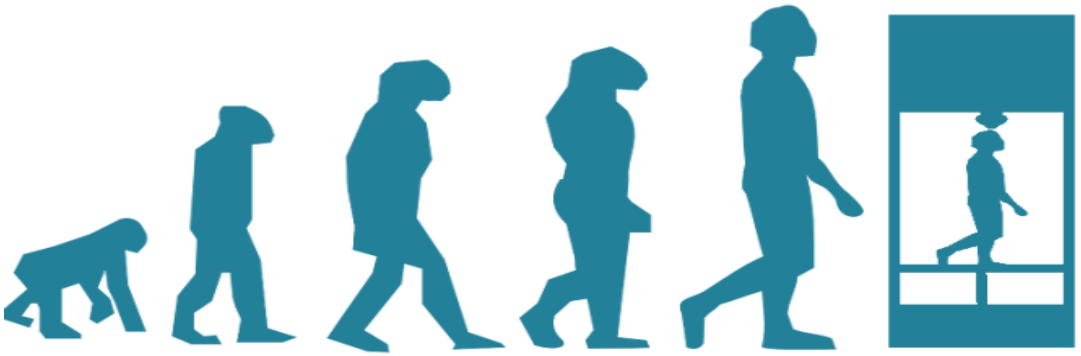
3D printing

3D printing today

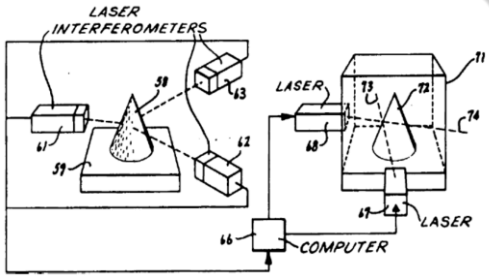
3D printing evolution



Doug Mancosky of printingDDD.com

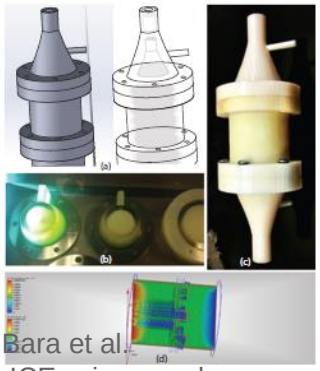
MASS PRODUCTION OR HI –TECH APPLICATIONS?

MAIN REQUESTS:



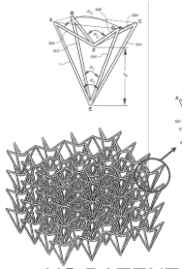
US PATENT 4041476 1977

3D PRINTERS TECHNOLOGY



Bara et al.
ICE science pub.

DESIGN



US PATENT 7910193

NEW FUNCTIONAL MATERIALS

3D printing technologies

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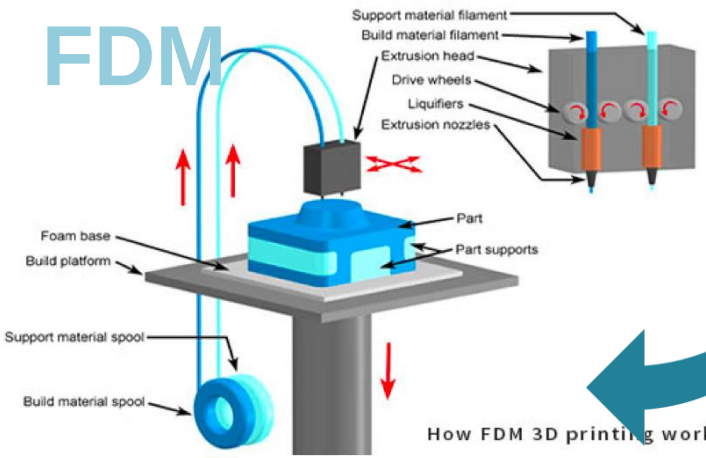
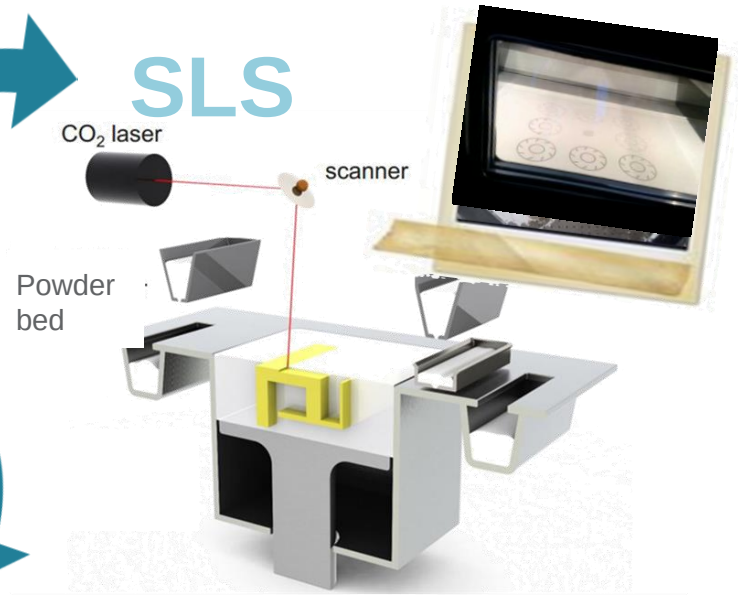
Different technologies

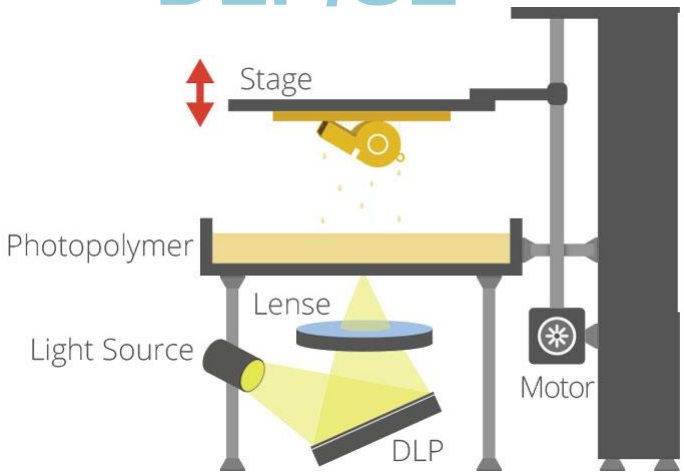
FDM

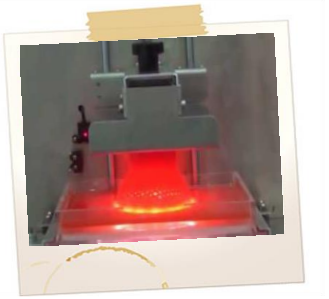


SLS



DLP/SL

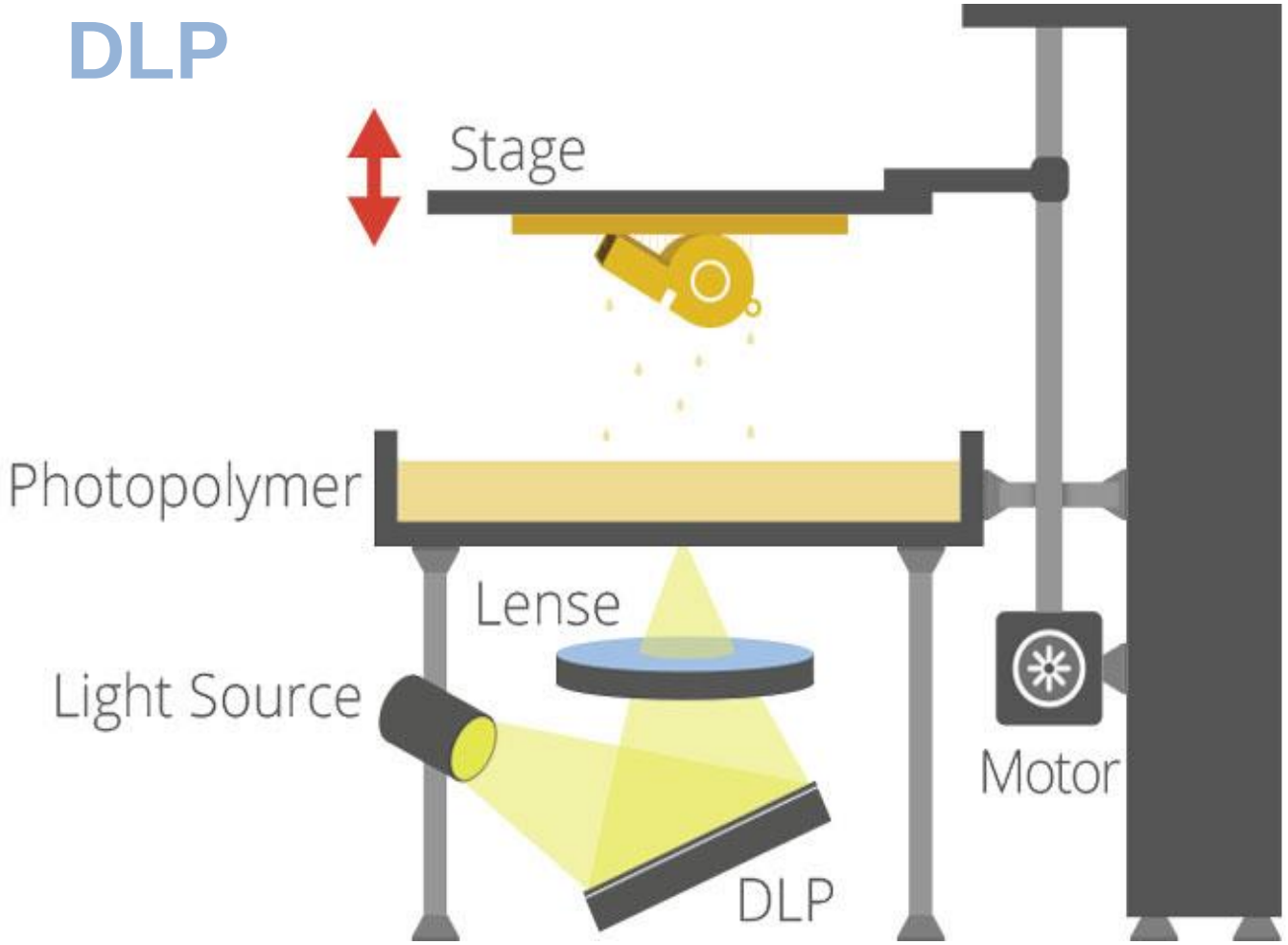




http://www.aniwaa.com/3d-printing-technologies-and-the-3d-printing-process/

3D printing technologies

DLP



Commercial DLP-3D printable formulations

Monomers

Initiators

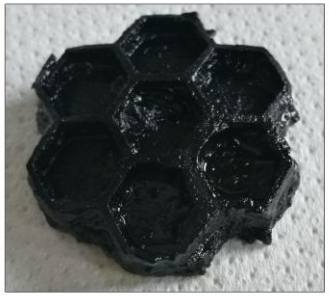
Dye

Addition of nanoparticles to obtain functional materials

Drawbacks:

- ✓ Increased formulation viscosity
- ✓ Limited light penetration depth
- ✓ Difficult nanoparticles dispersion
- ✓ Poor formulation stability

0.1% CNT



0.3% CNT

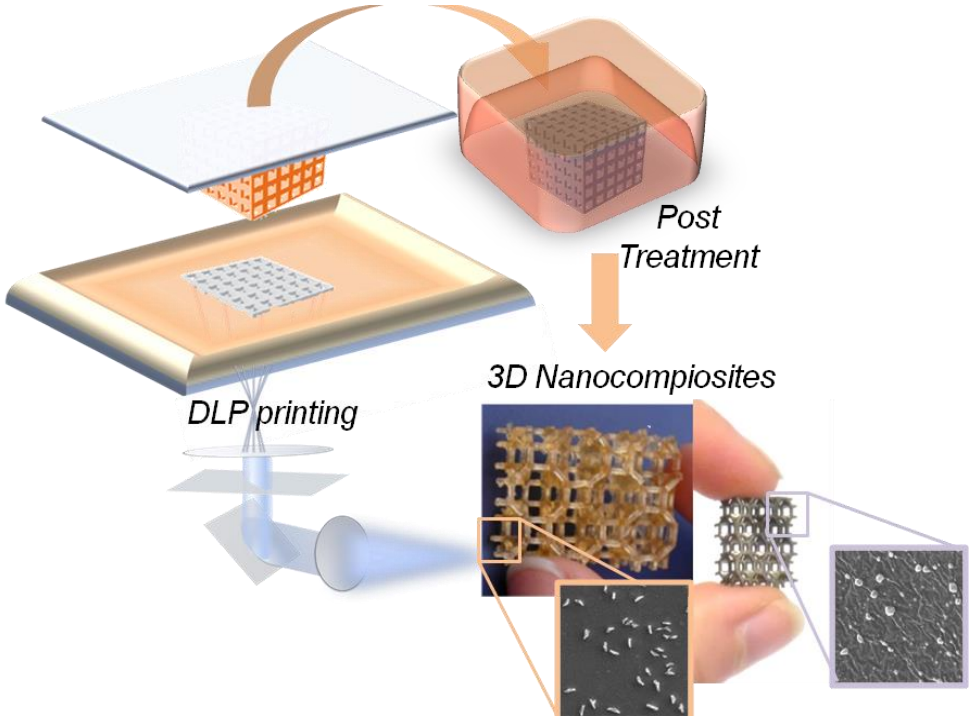
Proposed solution

BOTTOM- UP APPROACH

Addition of nanoparticles precursor to the printable formulations

+

post treatment on the printed pieces



EASILY PRINTABLE FORMULATIONS + FUNCTIONAL PRINTED OBJECTS

In situ generation of silica nanoparticles

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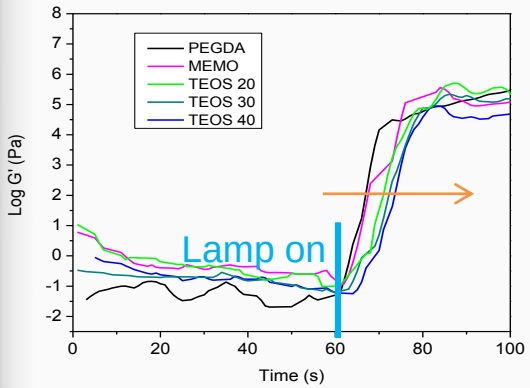
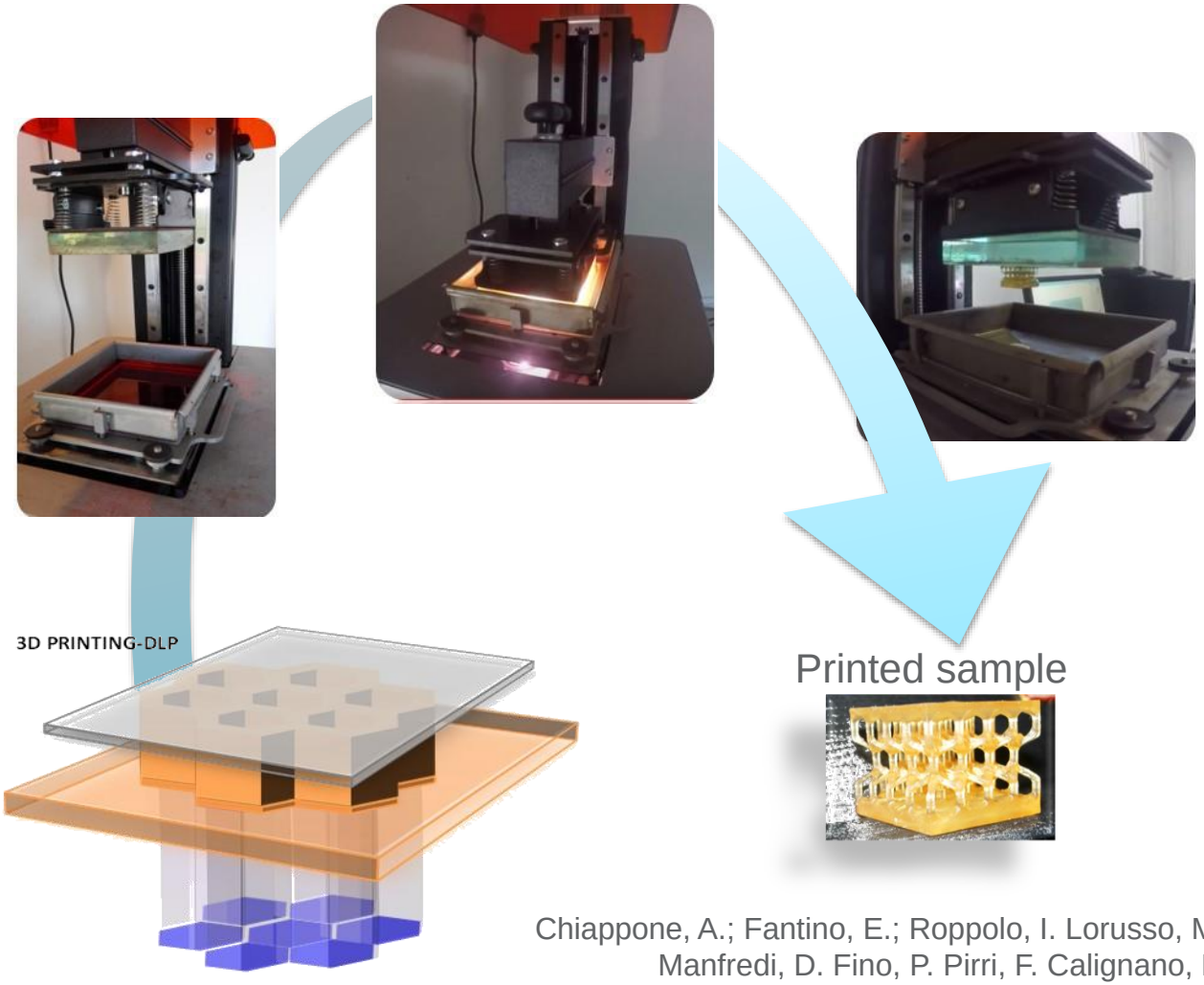
Addition of **TEOS** and **MEMO** to a **PEGDA** formulation

Preliminar Photorheology tests



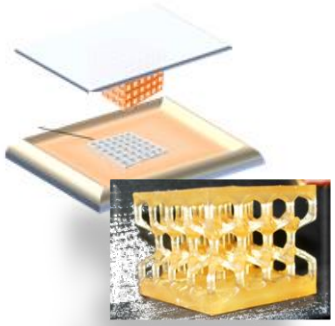
Teos content ↗
Irradiation time ↗

Initiators: Irgacure 819
Irgacure 1173

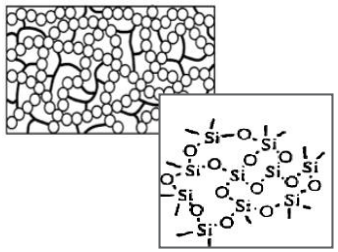


Chiappone, A.; Fantino, E.; Roppolo, I. Lorusso, M. Manfredi, D. Fino, P. Pirri, F. Calignano, F. **ACS Appl. Mat Interfaces 2016**, 8, 5627

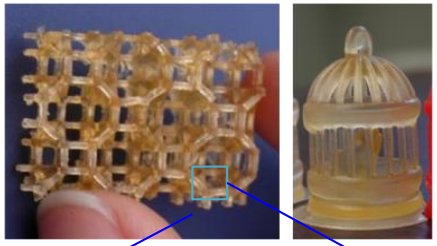
In situ generation of silica nanoparticles

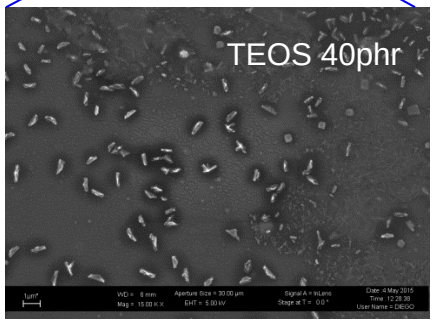


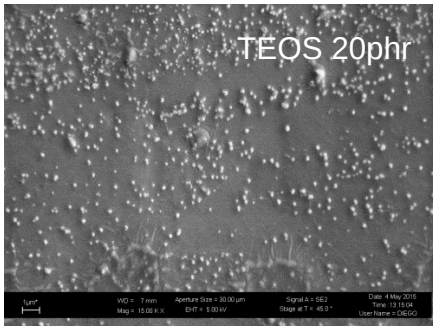
SOL-GEL

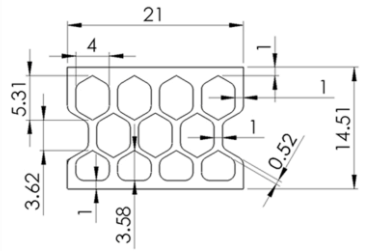


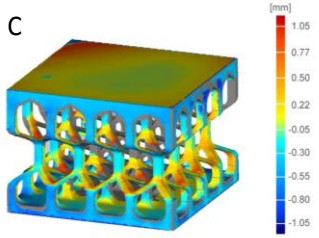
Formation of silica based hybrid nanocomposites











Sample	Tg (°C)	TGA residue (%)	Theoretical inorganic filler (%)
PEGDA	-41		
MEMO	-41	2.4	1.2
TEOS 20	-34	7.2	6.5
TEOS 30	-33	9	8.9
TEOS 40	-33	11.5	11.3

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In situ generation of silica nanoparticles

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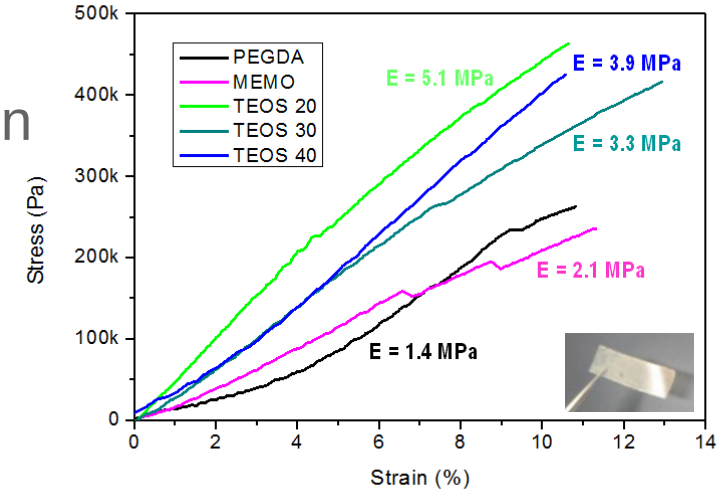
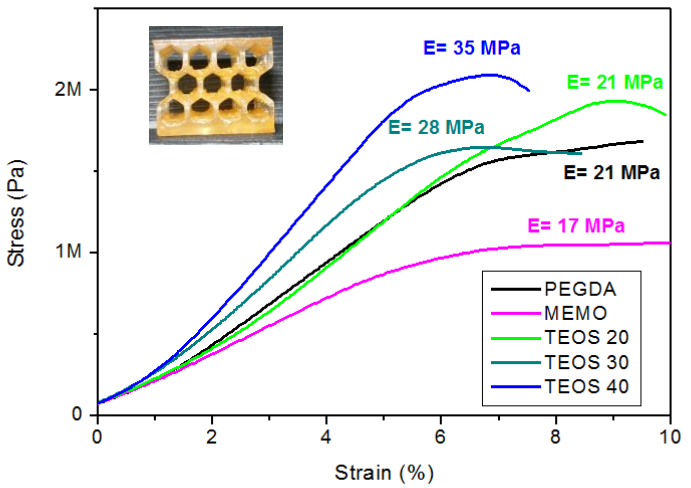
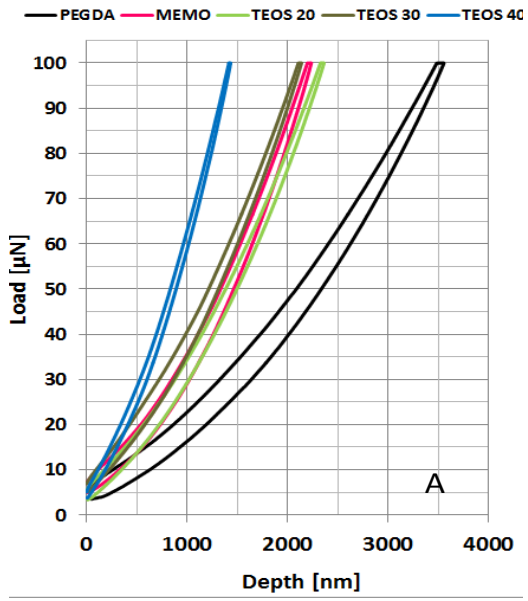
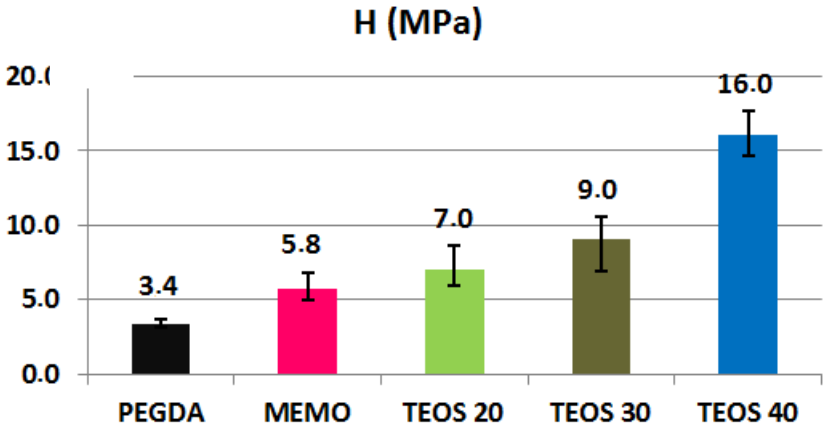
Tensile and compression tests







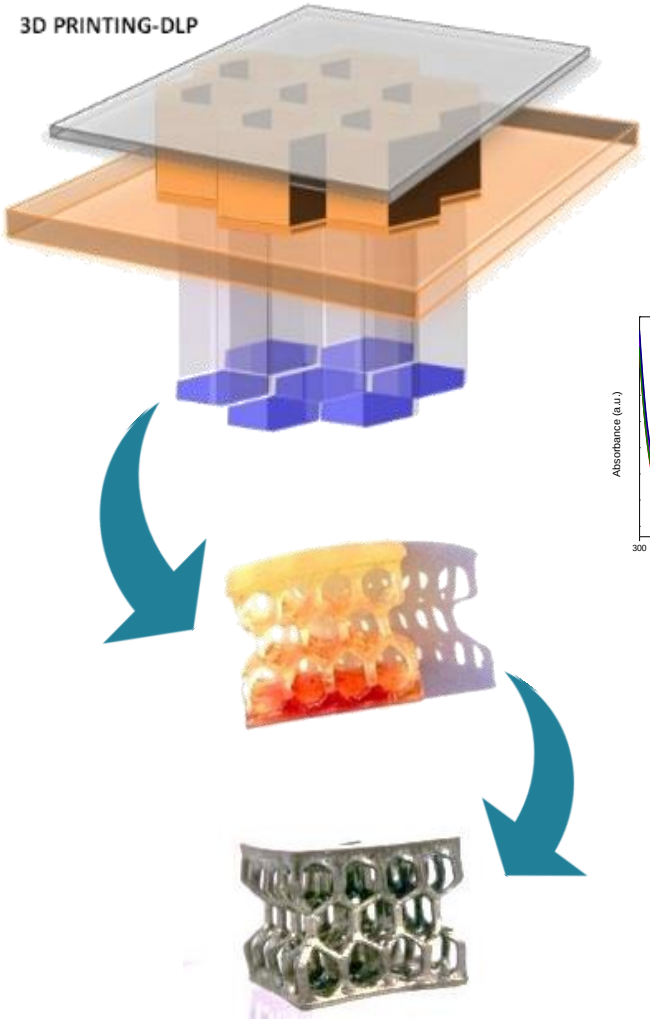
Nanoindentation test

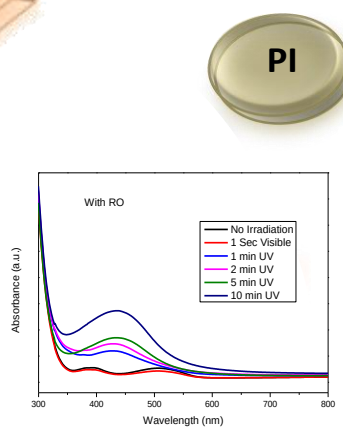


Chiappone et al. ACS Appl. Mat Interfaces **2016**, 8, 5627

In situ generation of silver nanoparticles

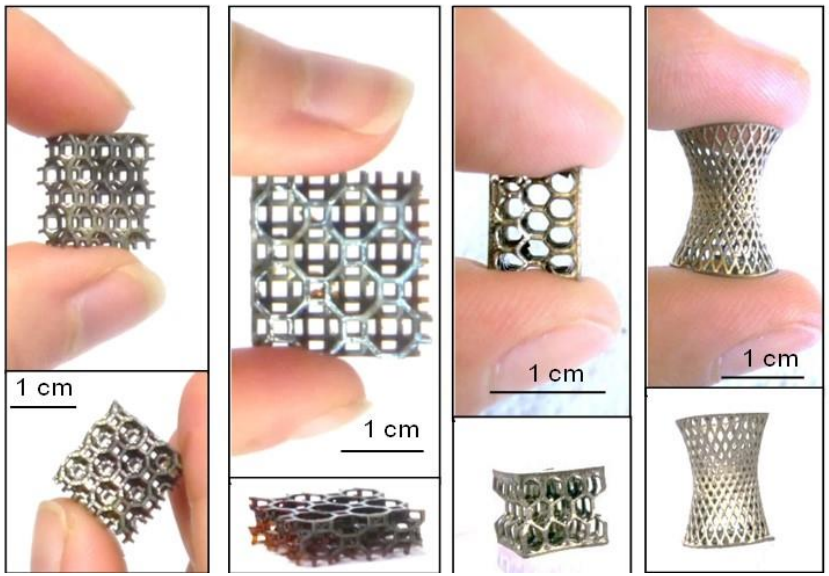
Addition of $AgNO_3$ salt to the PEGDA formulation





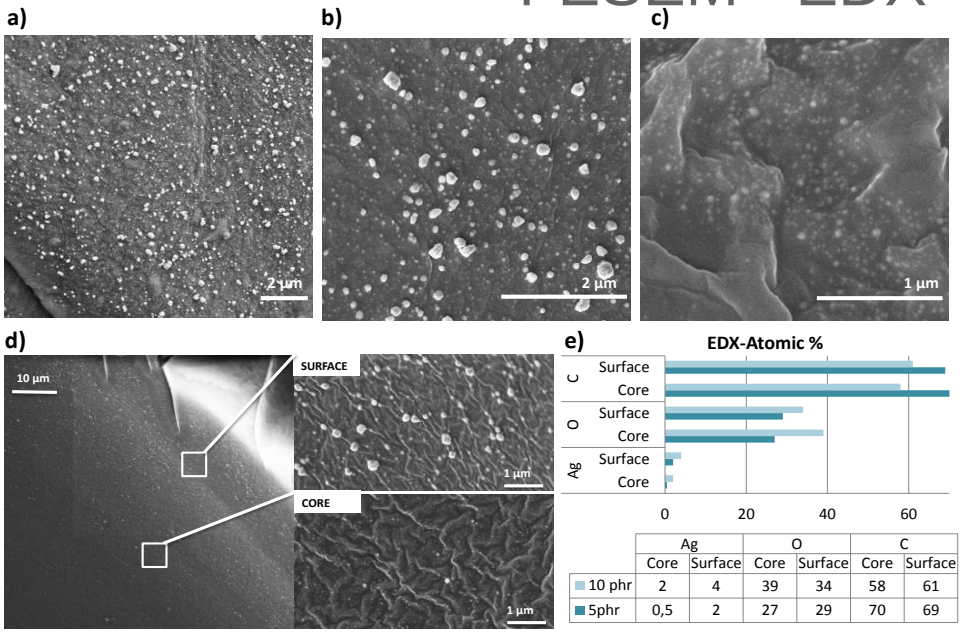
- *Fantino, E. Chiappone, A. Roppolo, I. Manfredi, D. Bongiovanni , R. Pirri, F. Calignano, F.* ***Adv Mat, 2016****. 28 (19),3712*
- *Fantino, E.; Chiappone, A.; Roppolo, I et al* ***Materials 2016****, 9(7), 589*

In situ generation of silver nanoparticles



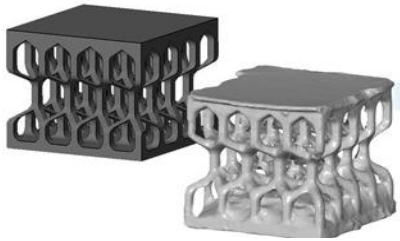
$AgNO_3$ (phr)	TGA Residue (%)	Theoretical Residue (%)	Tg (°C) (DSC)
0	0.7	0	-31
5	3.1	3	-29
10	5,9	6	-26
15	8,7	9	-29
20	10,57	12	-24

FESEM - EDX



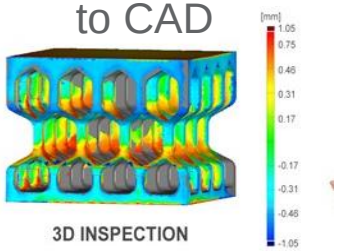
	Ag		O		C	
	Core	Surface	Core	Surface	Core	Surface
10 phr	2	4	39	34	58	61
5phr	0,5	2	27	29	70	69

CAD Model



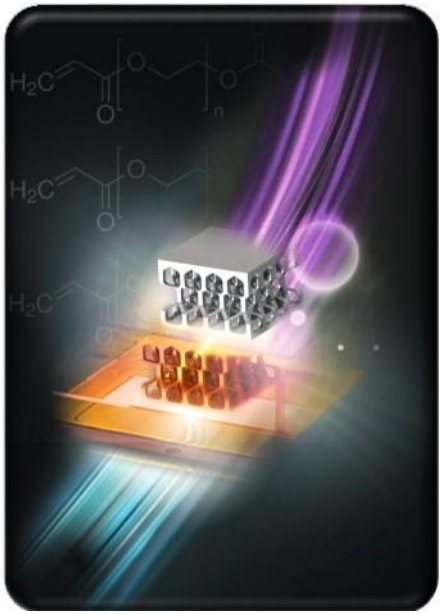
3D scanned DLP object

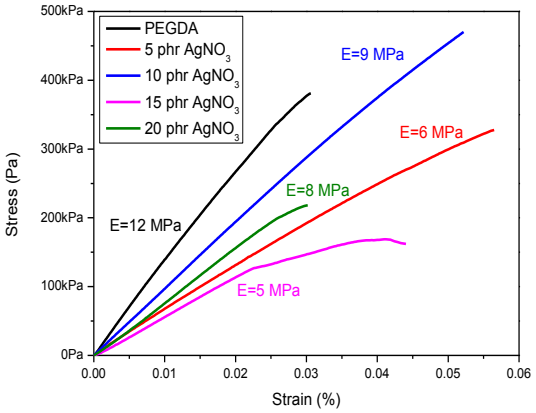
Good fidelity to CAD



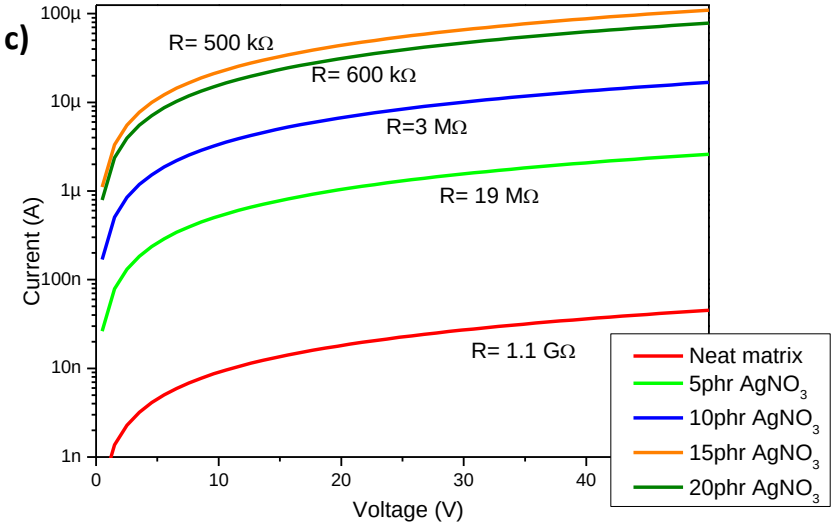
Fantino et al. **Adv Mat, 2016**. 28 (19),3712

In situ generation of silver nanoparticles





Sample	ρ (Ωcm)
PEGDA	2.6 *10^8
PEGDA $AgNO_3$ 5phr	4.5 *10^6
PEGDA $AgNO_3$ 10phr	7 *10^5
PEGDA $AgNO_3$ 15phr	1.1 *10^5
PEGDA $AgNO_3$ 20phr	1.5 *10^5



Fantino et al. **Adv Mat, 2016**. 28 (19),3712

In situ reduction of GO

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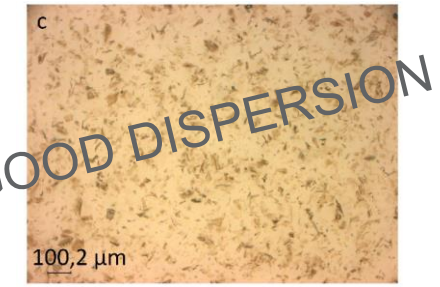
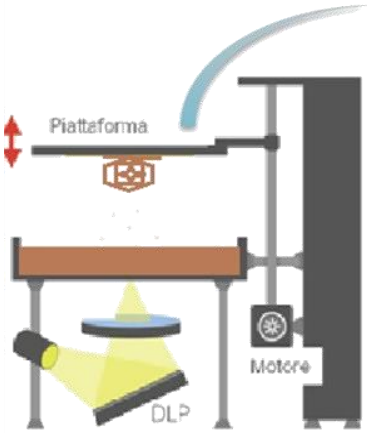
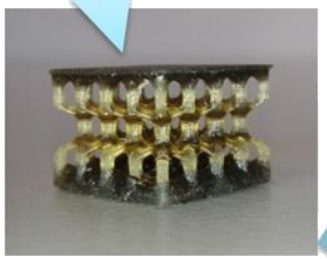
Addition of **GO** (0.3- 0.5 phr) to the PEGDA formulation using water as solvent

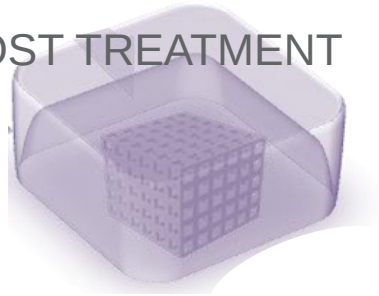


GOOD DISPERSION

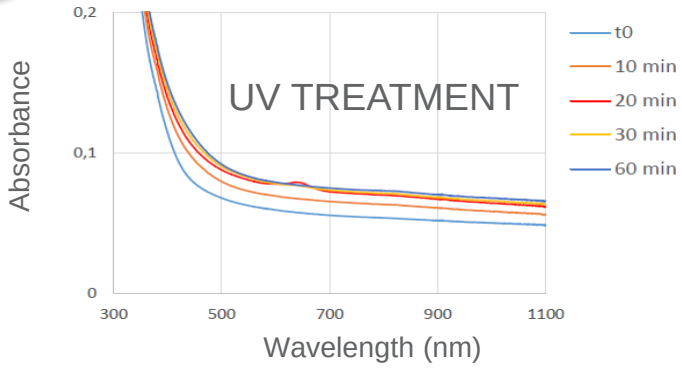




UV POST TREATMENT



UV-Vis spectroscopy



In situ reduction of GO

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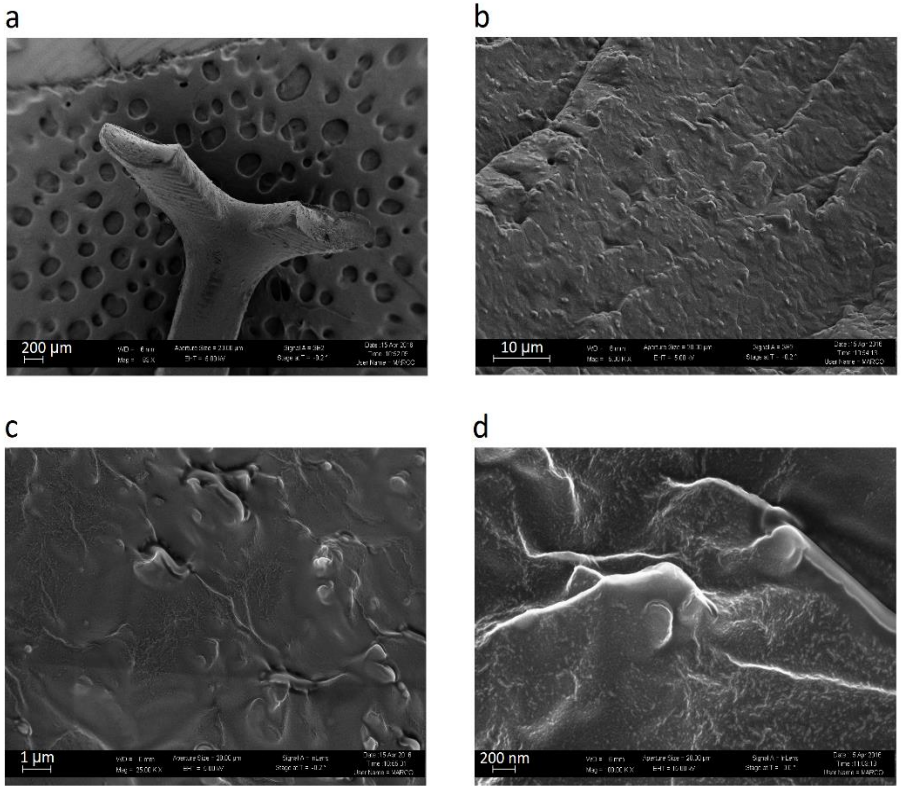
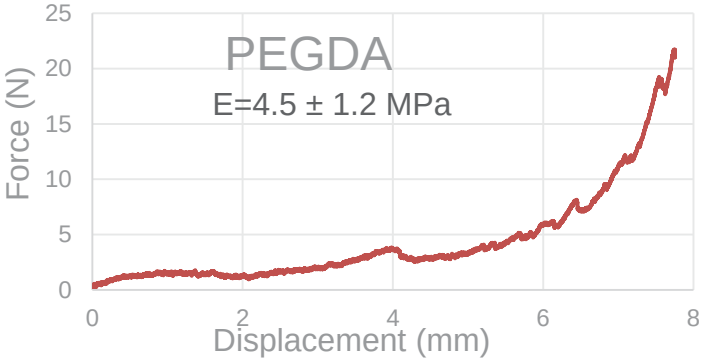
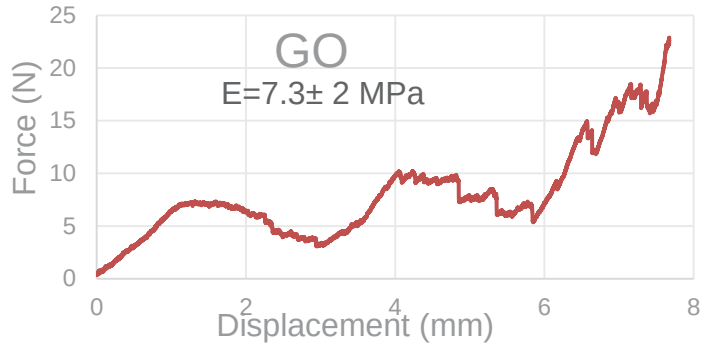
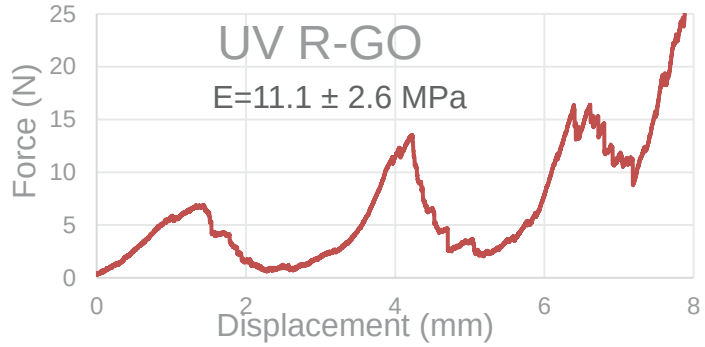
Compression test









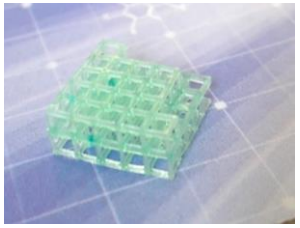
Other approaches

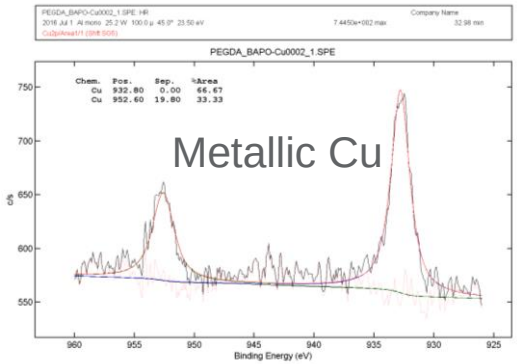
SPECIFCALLY DESIGNED PHOTOINITIATORS

ETH zürich
Grützmacher group

Cu(II)-BAPO-complex

PEG-diacrylate monomer



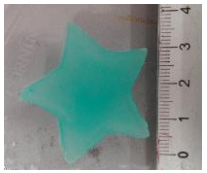


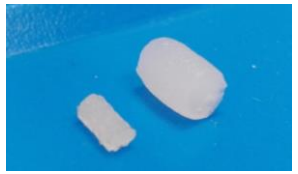
Copper nanoparticles in situ formation
High printing resolution
Microbial applications

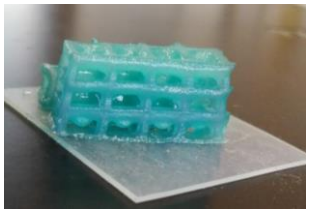
BAPO functionalized CelluloseNCs

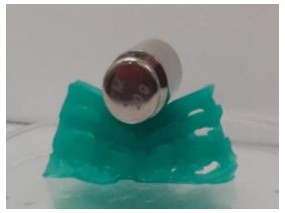
PEG-monoacrylate monomer

3D printable hydrogels with outstanding water uptake





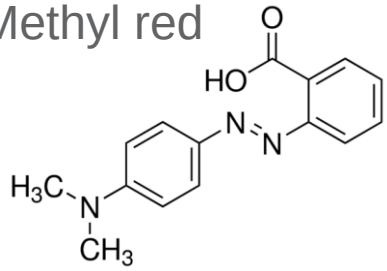




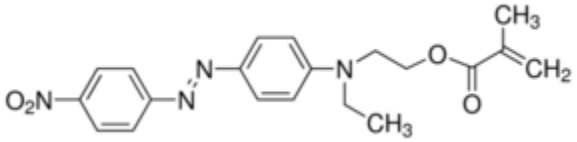
Other approaches

USE OF PHOTOSENSITIVE MOLECULAR SWITCHES AS DYE

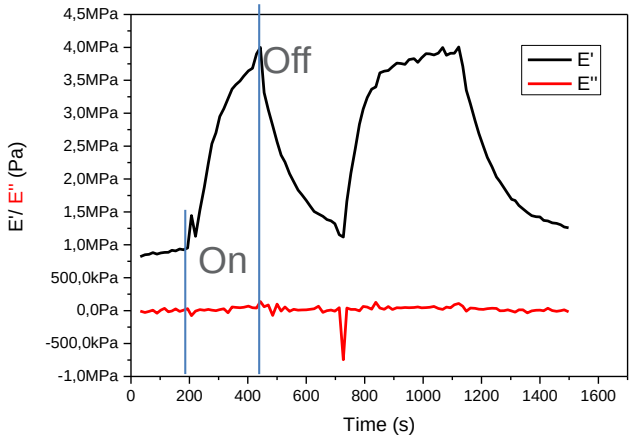
Methyl red

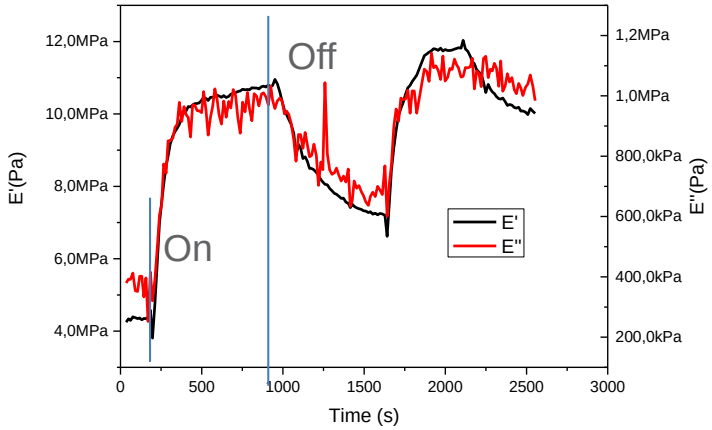


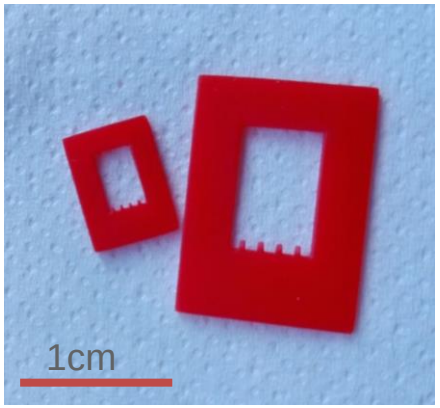
Dispersed red methacrylate



PEG-diacrylate monomer





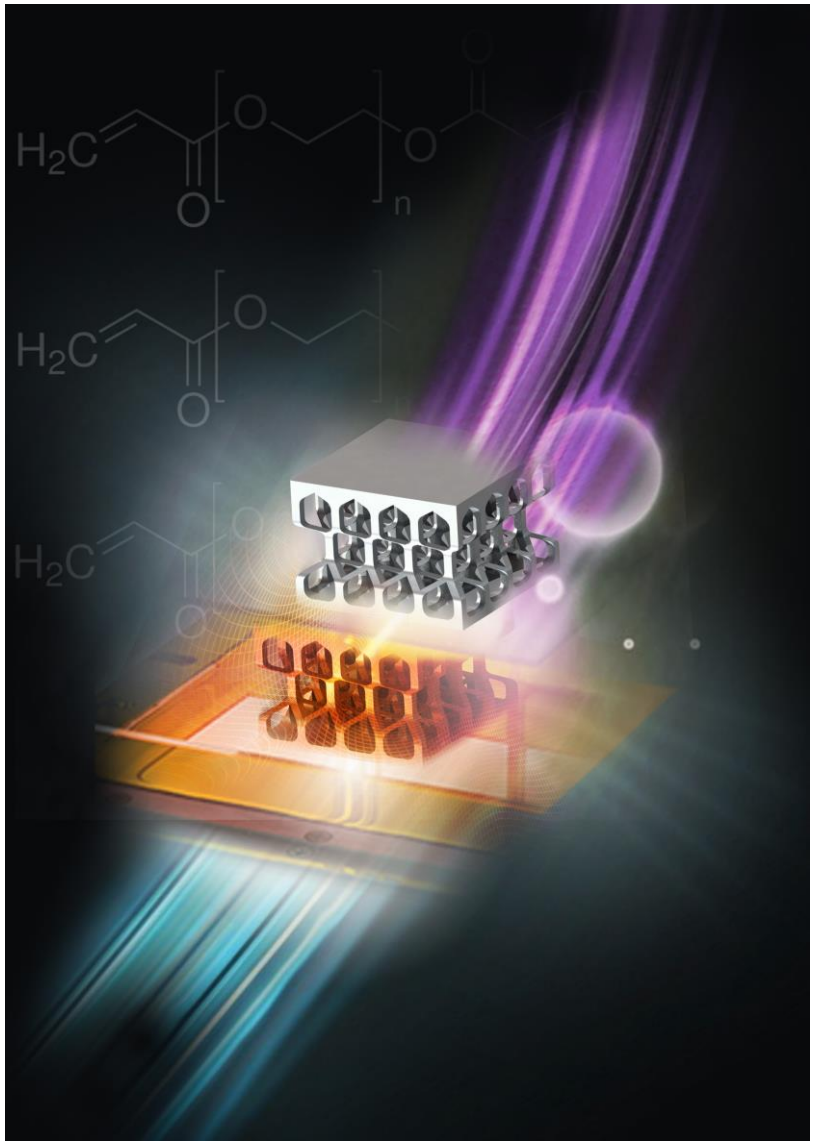


Modification of the mechanical response of the polymer upon laser illumination (532 nm)

Conclusion

Easily printable formulations

Functional printed objects



THANK YOU!

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