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NANOSCIENCES

2nd year PhD report

Supervisor: Andrea Camposeo

Pisa, 17/10/2019

Francesca D'Elia

Work Plan

ATTENDED COURSES (with final exam)

Biophysical Sciences (Prof. F. Cardarelli)

RESEARCH PRODUCTION

Szukalski, A., Uttiya, S., **D'Elia, F.**, Portone, A., Pisignano, D., Persano, L., and Camposeo, A. "3D photo-responsive optical devices manufactured by advanced printing technologies", Proc. SPIE vol. 10915, Art. N. 1091503 (2019).

Portone, A., **D'Elia, F.**, Romano, L., Szukalski, A., Matino, F., Fabbri, F., Persano L, Pisignano D, Camposeo A., "Shaping of photo-active materials by 3D printing", NOMA. NoM2B.3 (2019).

Research objectives

PhD GOAL: **Development of 3D printed responsive components driven by light**

OBJECTIVE 1: Additive manufacturing of **optical systems** by 3D printing methodologies based on stereolithography (**SLA**) and Digital Light Processing (**DLP**).

OBJECTIVE 2: Study of the optical properties of 3D printed materials embedding **photo-luminescent** and **photo-responsive** molecules.

1. Methodologies for 3D printing

UV light sources are used to induce photo-polymerization of liquid pre-polymers

Design of the object

Slicing of the 3D model

PROCESS PARAMETERS

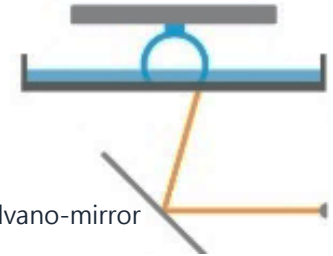
- Thickness of the single layer

Selective exposure to UV light by a scanning **laser** (wavelenght 405 nm)

PROCESS PARAMETERS

- Laser scanning rate
- Laser power ratio
- Weight ratio between photoiniziator and monomer

SLA

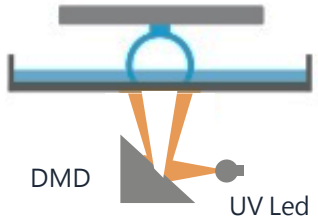


Selective exposure to 405 nm light by a **LED**-illuminated digital micro-mirror array (DMD projector)

PROCESS PARAMETERS

- Exposure Time
- Weight ratio between photoiniziator and monomer

DLP

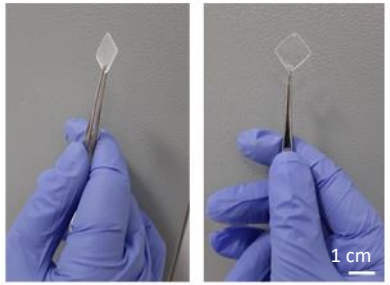


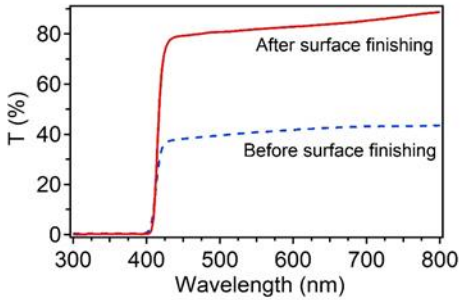
1. Methodologies for 3D printing

- ✓ High design flexibility
- ✓ Possibility of printing optical systems

- ✗ Low intensity of visible light transmitted by the printed structures (I_t/I_0: max 50% in the visible range, 400 – 800 nm)
- ✗ Undesired absorption & emission of UV light by **additives** in commercially available transparent pre-polymers

Post-Printing Surface Finishing

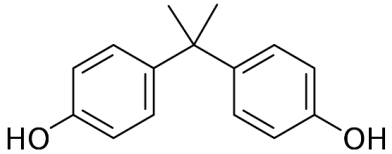




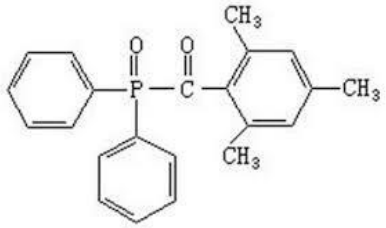
Engineered pre-polymer

Monomer & Photo-iniziator

Bisphenol A



TPO



1. Methodologies for 3D printing

1.1. Material: E-Shell600 ® EnvisionTEC

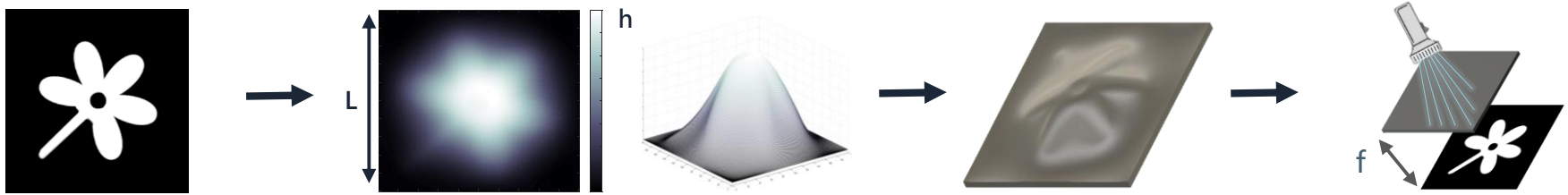
In collaboration with Prof. A. **Tredicucci**

I. Design of the pattern

II. Lens design

III. Lens fabrication

IV. Lens characterization



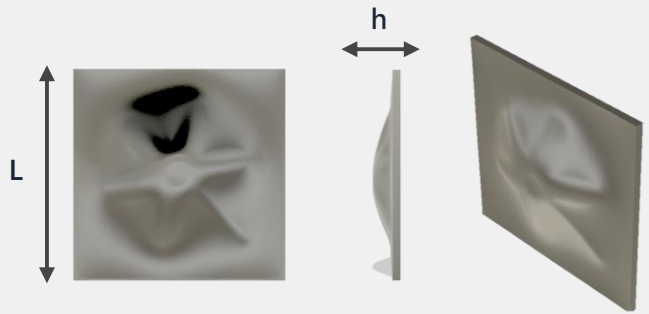
@F. Pisani

SLA

DESIGN

L = 40 mm
h = 10 mm

Focal distance:
3 cm

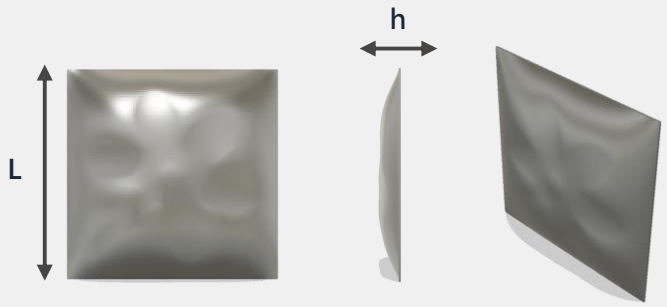


DLP

DESIGN

L = 27 mm
h = 3 mm

Focal distance:
1 cm



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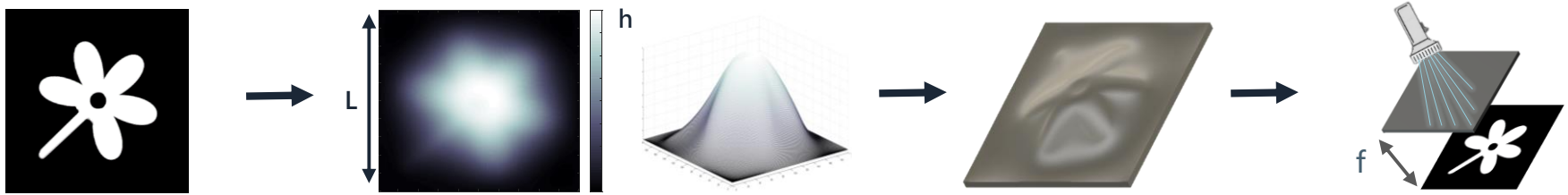
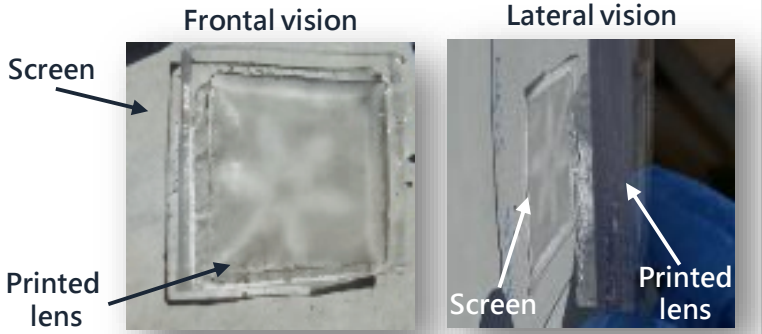
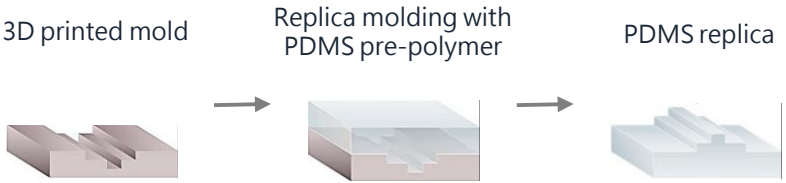


@F. Pisani

DLP Single layer thickness: 15 μm
Focal distance: 1 cm



Work in progress: Replica molding of 3D printed template



Goal: variation of the displayed pattern by mechanical elongation of the elastomeric lens

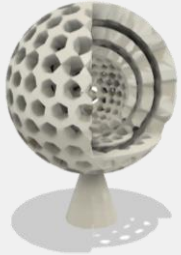
1. Methodologies for 3D printing

SLA

1.2. Material: Bisphenol A + 5 % TPO (% wt/wt)

DESIGN

Ø ext = 20 mm
h = 33 mm

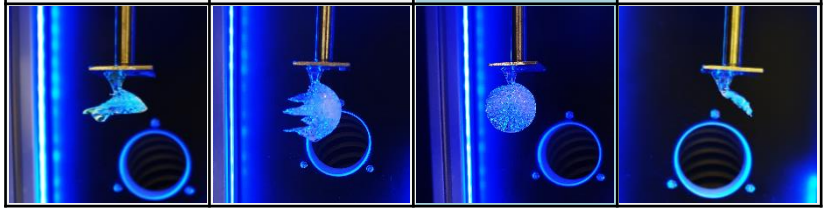


PARAMETERS

- Single layer thickness : 100 µm
- Laser scanning rate: 150.000 µm/s

Laser power ratio (%)

20	30	40	50



DLP

1.2. Material: Bisphenol A + 1 % TPO (% wt/wt)

DESIGN

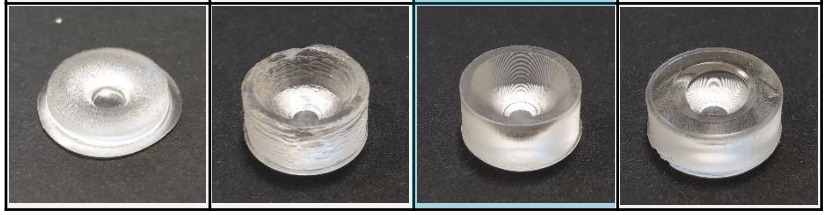
Ø ext = 10 mm
Ø int = 2 mm
h = 5 mm

PARAMETERS

- Single layer thickness: 50 µm

Exposure time (s)

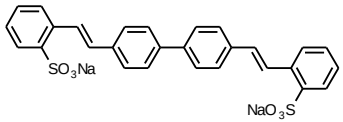
3	3.5	4	5



2. Photo-responsive 3D printed polymers

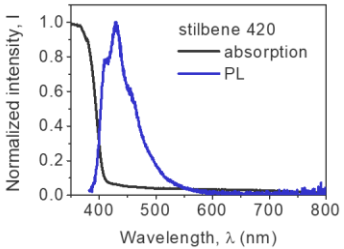
2.1. Material: light emitting molecules embedded in 3D printed polymer

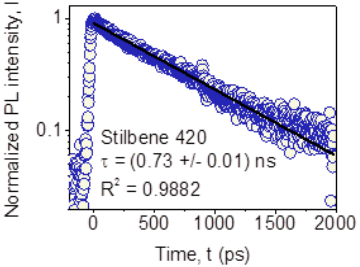
Stilbene-420



3D printed single layer (SLA)

BPA + 5%TPO + 0.1% SB-420

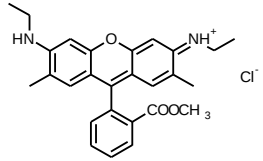




Compound	Stilbene 420
ABS I_{max} (nm)	363.3±1.0
I_{exc} (nm)	375.0
PL I_{max} (nm)	430.7±1.0
SS[a], Dl (nm)	67.4±1.0
Φ_p (%) Printed	53.1
Φ_W (%) PVA Water	91.1
Φ_O (%) PMMA	17.8
t (ns)	0.73
k_r (ns^{-1})	0.73
k_{n-r} (ns^{-1})	0.64

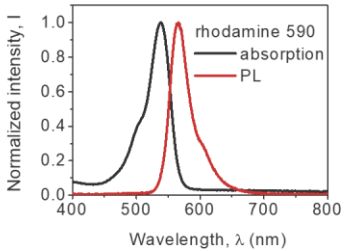
@A. Szukalski

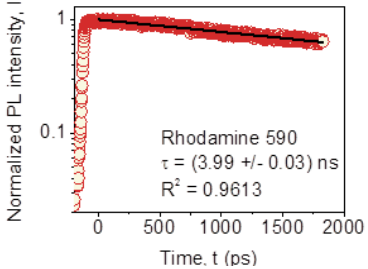
Rhodamine-590



3D printed single layer (SLA)

BPA + 5%TPO + 0.1% RD-590





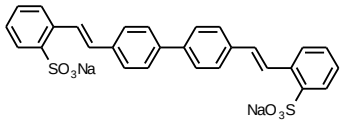
Compound	Rhodamine 590
ABS I_{max} (nm)	537.8±1.0
I_{exc} (nm)	488.0
PL I_{max} (nm)	565.4±1.0
SS[a], Dl (nm)	27.6±1.0
Φ_p (%) Printed	72.1
Φ_W (%) PVA Water	32.1
Φ_O (%) PMMA	46.5
t (ns)	3.99
k_r (ns^{-1})	0.03
k_{n-r} (ns-1)	0.22

@A. Szukalski

2. Photo-responsive 3D printed polymers

2.1. Material: light emitting molecules embedded in 3D printed polymer

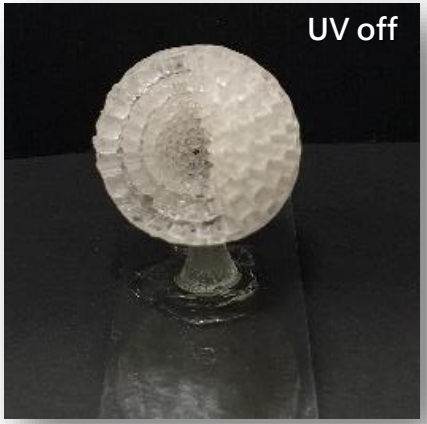
Stilbene-420



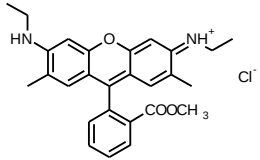
3D printed single layer (SLA)

BPA + 5%TPO + 0.1% SB-420

3D printed structure



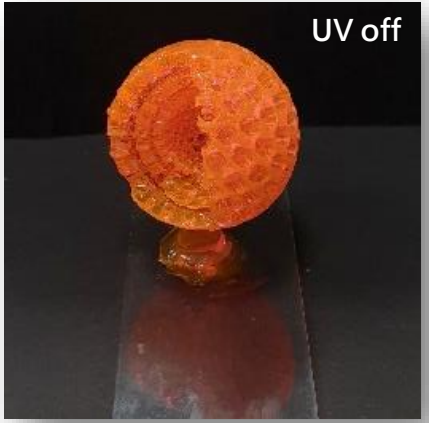
Rhodamine-590



3D printed single layer (SLA)

BPA + 5%TPO + 0.1% RD-590

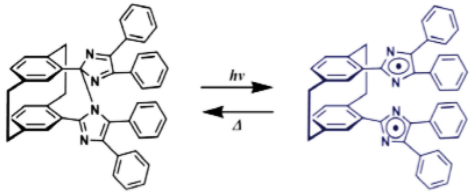
3D printed structure



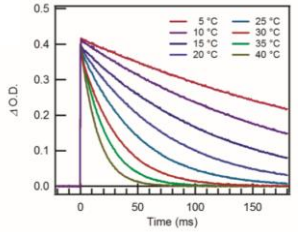
2. Photo-responsive 3D printed polymers

2.2. Material: Fast Photochromic molecules embedded in 3D printed polymer

Pseudogem-bisDPI[2.2]PC



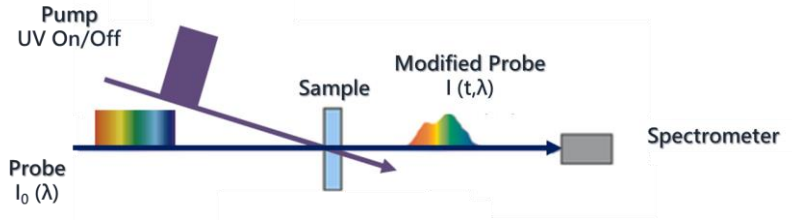
COLORLESS COLORED



Decay profiles of the colored species generated from pseudogem-bisDPI[2.2]PC

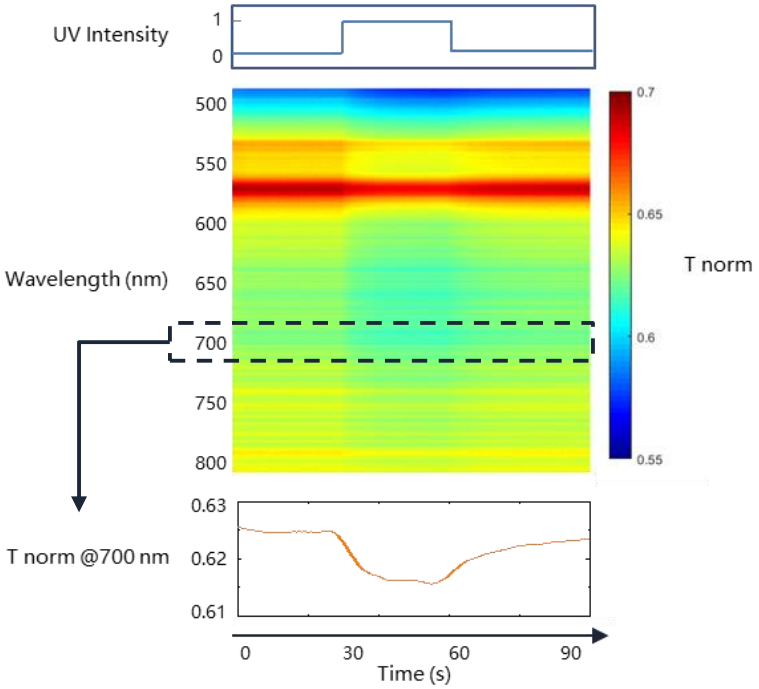
A Fast Photochromic Molecule That Colors Only under UV Light
Yuta Kishimoto and Jiro Abe
J. AM. CHEM. SOC. 2009, 131, 4227–4229

Pump-probe absorption set-up



Pump-probe absorption of 3D printed single layer

BPA + 1%TPO 5% PC



Future work

- **Morphological characterization** of the printed structures (SEM, AFM);
- Characterization of **projected patterns** of 3D printed complex lenses @ various wavelengths (400-1500 nm);
- Investigation of photo-polymerization kinetics and of the properties of the embedded molecules by **Raman spectroscopy**;
- Study of the **photo-switching properties** (characteristic switching times, number of cycles, fatigue properties) of photochromic molecules in 3D printed objects;
- Study of the **photo-luminescence properties** (photo-stability, number of ON-OFF cycles, fatigue properties) of light emitting molecules in 3D printed objects;

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Thanks for the attention

Francesca D'Elia