Two-photon polymerized microstructures for photonics and biomedical applications

D. S. Corrêa[1,2], P. Tayalia[2], T. Voss[2], E. Mazur[2] and C. R. Mendonca[1,2]

[1]Instituto de Física de São Carlos,Universidade de São Paulo, São Carlos, SP, Brazil,
[2]Department of Physics, Harvard University,, Cambridge, MA, USA
crmendon@if.sc.usp.br
www.fotonica.ifsc.usp.br

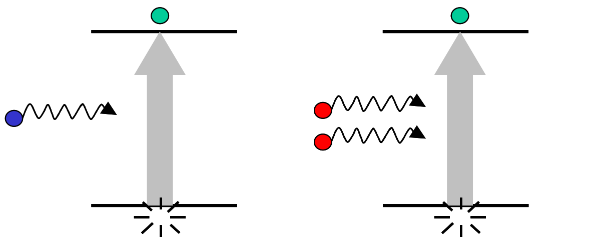
Motivation

Two-photon absorption (2PA) polymerization has been shown to be a useful tool in the 3D-fabrication of micro- and nanostructures. The nonlinear nature of the multiphoton absorption confines the polymerization to the tiny focal volume of the pumping laser, allowing the fabrication of complex microstructures. In this work we describe the fabrication of microstructures employing polymeric blends in a guest/host scheme. We used mixture of acrylate resins as polymeric host and Lucirin TPO-L as photoinitiator. As guest material, we employed: (i) MEH-PPV and (ii) Chitosan.

We fabricated MEH-PPV-containing microstructures and obtained fluorescence microscopy images, which display the typical fluorescence spectrum of MEH-PPV. We also demonstrated waveguiding by 100-μm long structures containing MEH-PPV, with potential applications in photonics devices.

We also used this doping approach to fabricate microstructures containing chitosan. We verified that this biopolymer remains into the microstructure, without forming any crosslinking with the acrylic resins. Besides, chitosan does not impair the mechanical properties of the resin. The addition of drugs (*e.g.*antibiotics) to the base material used in the microfabrication is also feasible, opening new venues in advanced drug delivery and tissue regenerating systems.

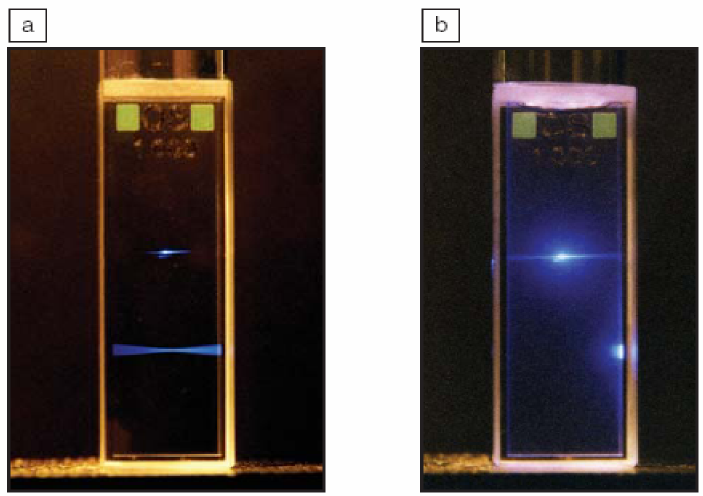
Two-photon absorption (2PA)



Two photons are absorbed in a single event

Advantage of the process:

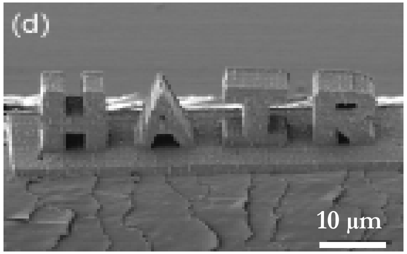
Spatial selectivity in the process



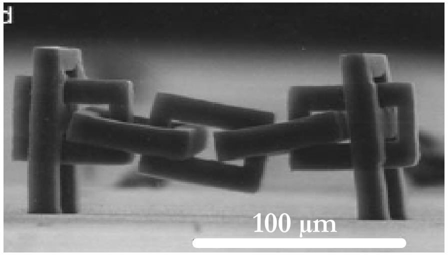
Perry, J.W. et al. MRS Bulletin, 2007

2PA applications

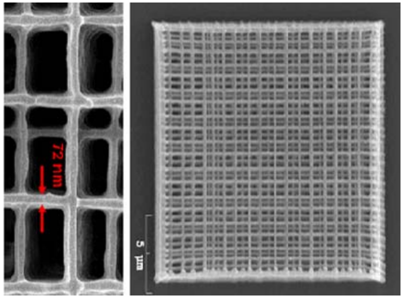
- 2PA fluorescence microscopy
- Optical limiting
- Photodynamic therapy
- Fabrication of microdevices via 2PA polymerization



T. Baldacchini et al; *J. Appl. Phys.* 2004

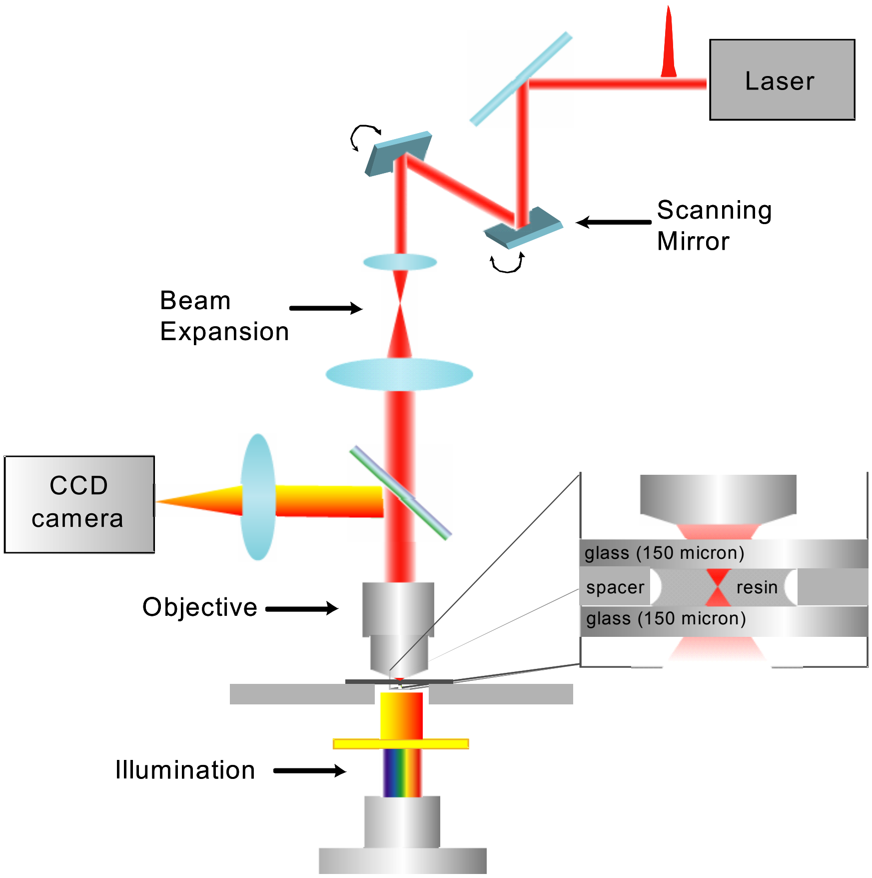


J. W. Perry et al; *J. Phot. Sci. Tech.* 2001



J. W. Perry et al; Opt. Exp. 2007

2PA polymerization setup



Ti:sapphire laser oscillator

- 130 fs
- 800 nm
- 76 MHz
- 20 mW

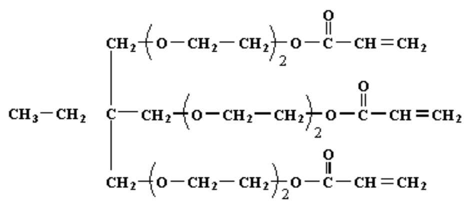
Objective

40 x
0.65 NA

Monomers and photoinitiator

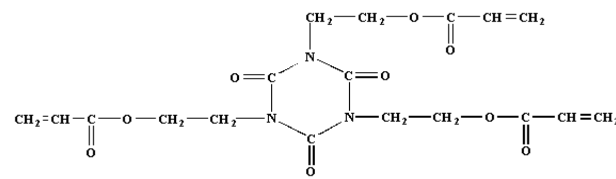
Monomers

SR499



Decreases residual stress during shrinkage

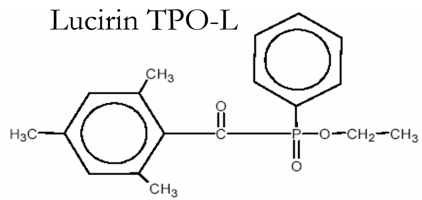
SR368

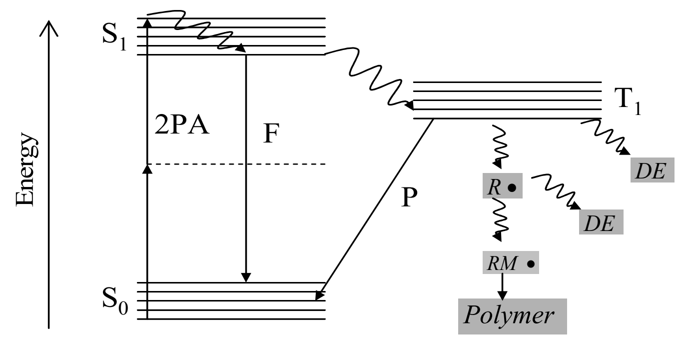


Provides hardness to the polymeric structure

Photoinitiador

Lucirin TPO-L

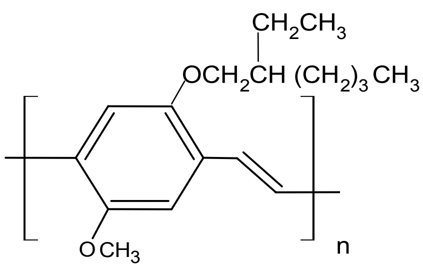




“Doping” materials: MEH-PPV and Chitosan

MEH-PPV

Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene)

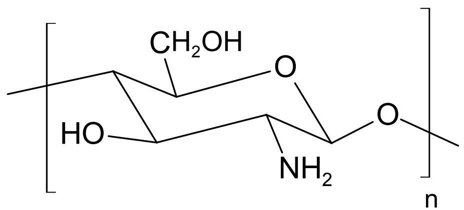


Why adding MEH-PPV to the acrylic resin?

- → π-conjugation along the polymer backbone
- → High optical nonlinearities
- → Photo and electroluminescence
- → Application in photonics related areas

Chitosan

[(1→4)-2 amino –2 –deoxy-β-D-glucan]

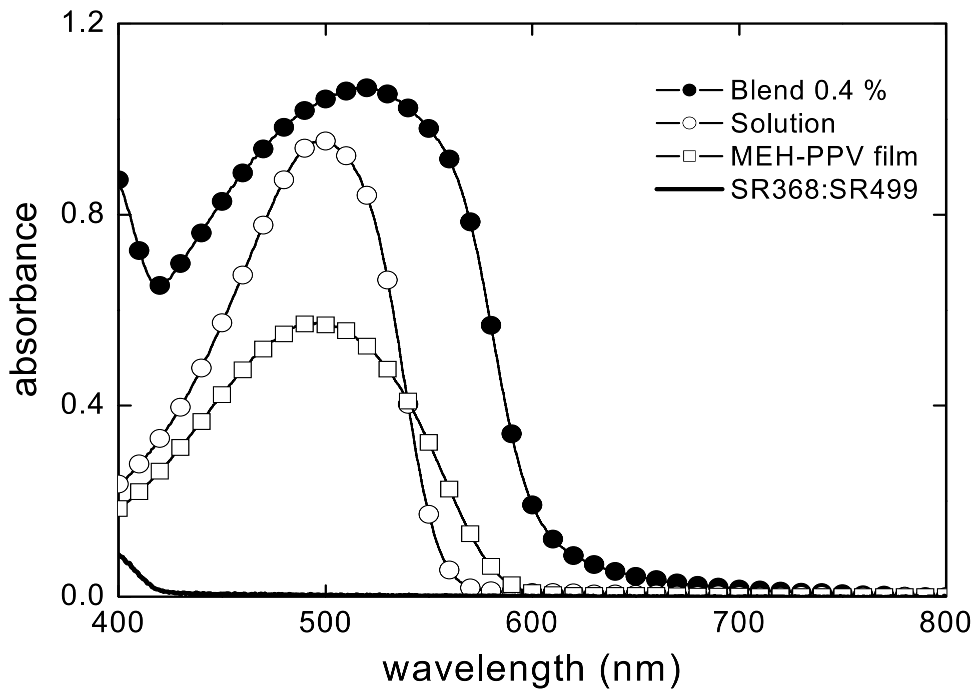


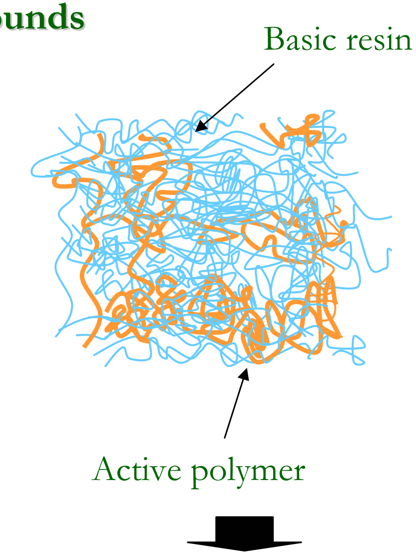
Why adding chitosan to the acrylic resin?

- → Bio degradable and bio compatible
- → Use as taste sensor, blood coagulation
- → Application in medical related areas, such as bone replacement, tissue engineering, etc

Microstructures containing MEH-PPV

Absorption spectrum of the MEH-PPV and its compounds

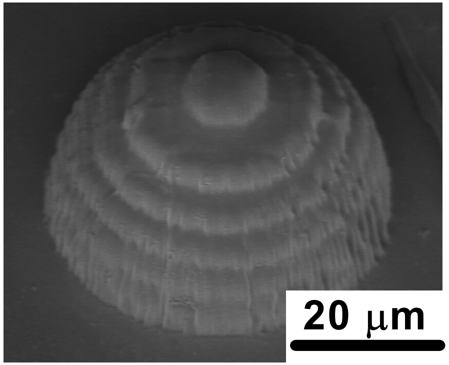


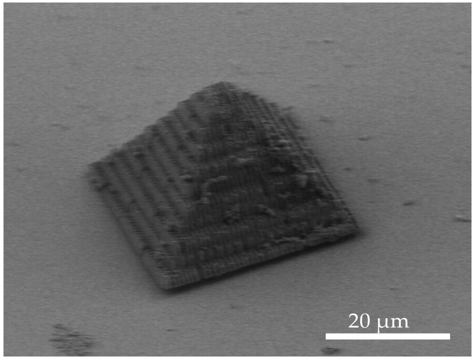


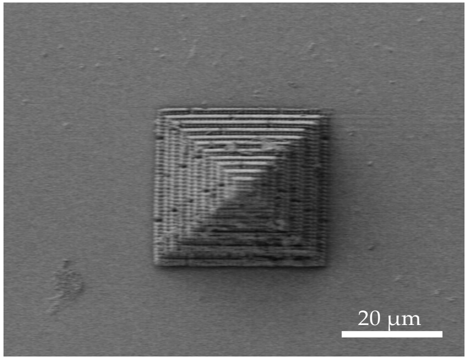
Fluorescence
Electro Luminescent
Conduction

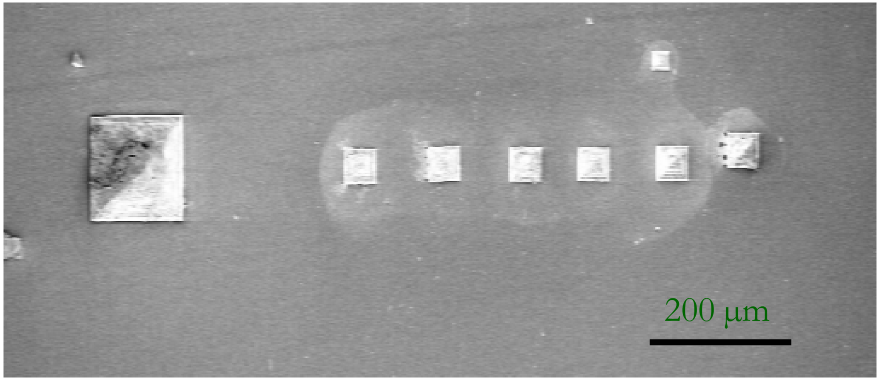
Microstructures containing MEH-PPV

SEM of some fabricated microstructures



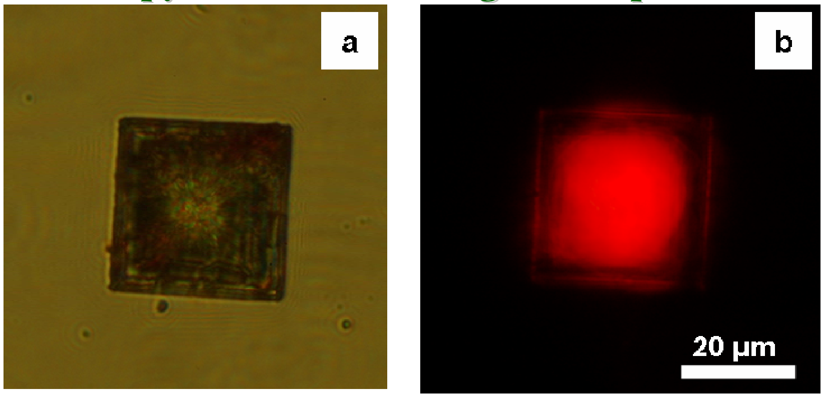




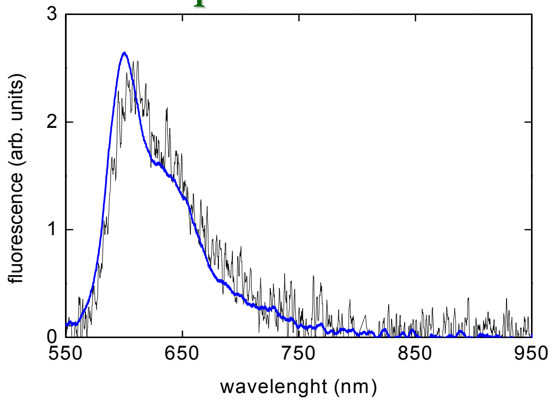


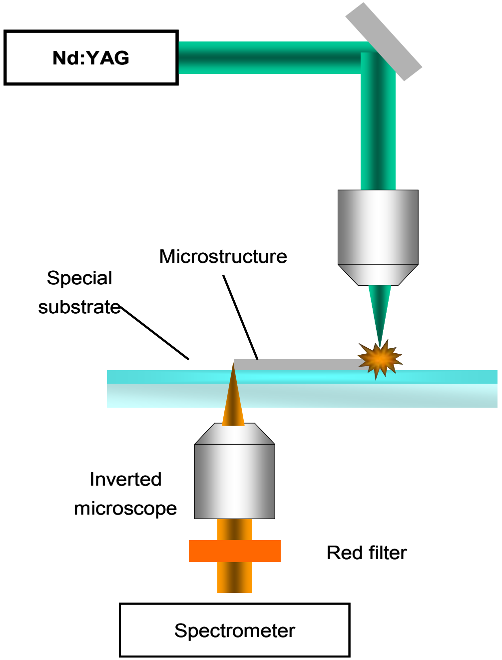
Microstructures containing MEH-PPV

Microscopy fluorescence images of doped microstructures



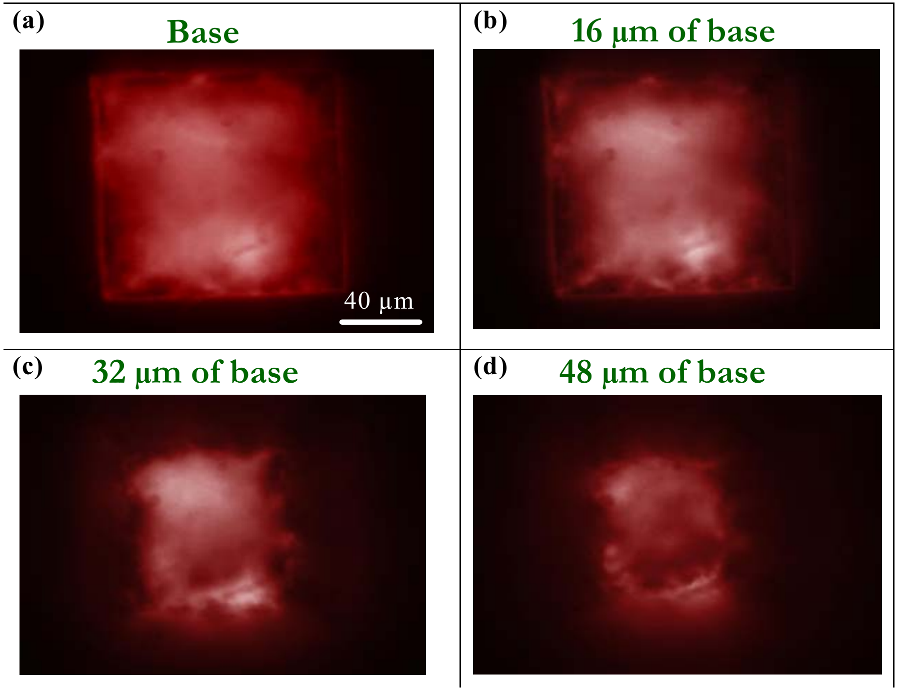
Fluorescence spectrum of the microstructure

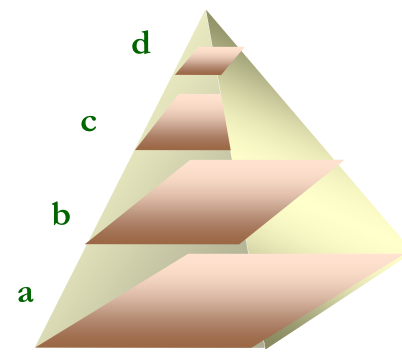




Microstructures containing MEH-PPV

Distribution of MEH-PPV into the microstructure

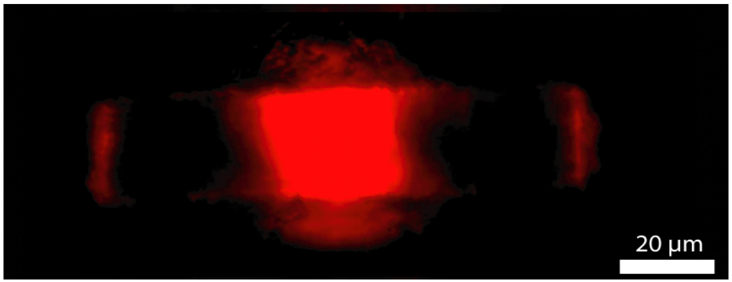


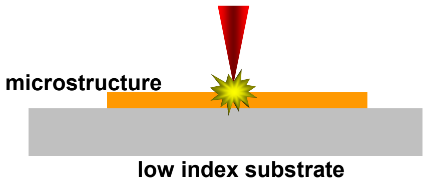


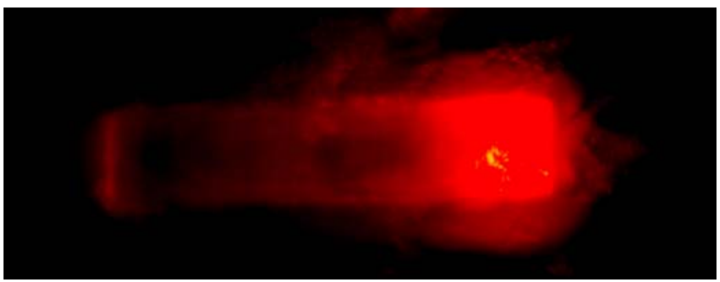
Confocal microscopy of the microstructure sections

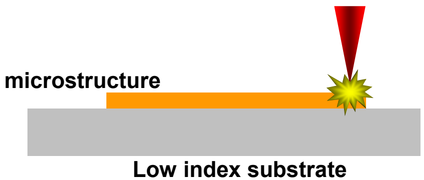
Microstructures containing MEH-PPV

Waveguides made with acrylic resins and 1% of MEH-PPV







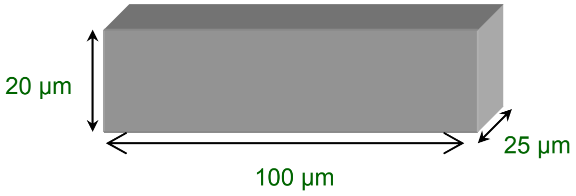


Substrate of mesoporous silica:

8 nm-pores filled with air (n = 1.185)

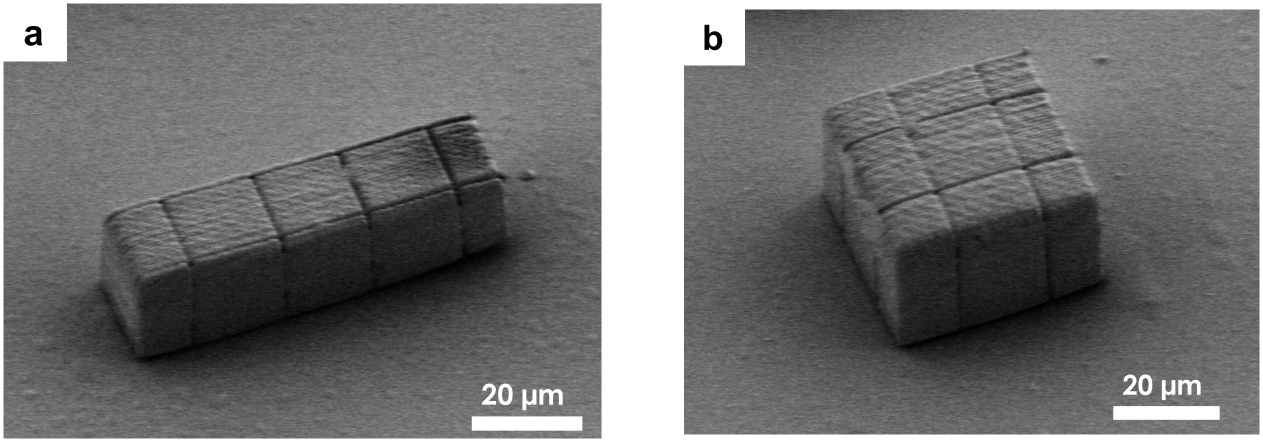
-Minimize light scattering

-Avoid scattering and couple of light with the glass



Microstructures containing chitosan

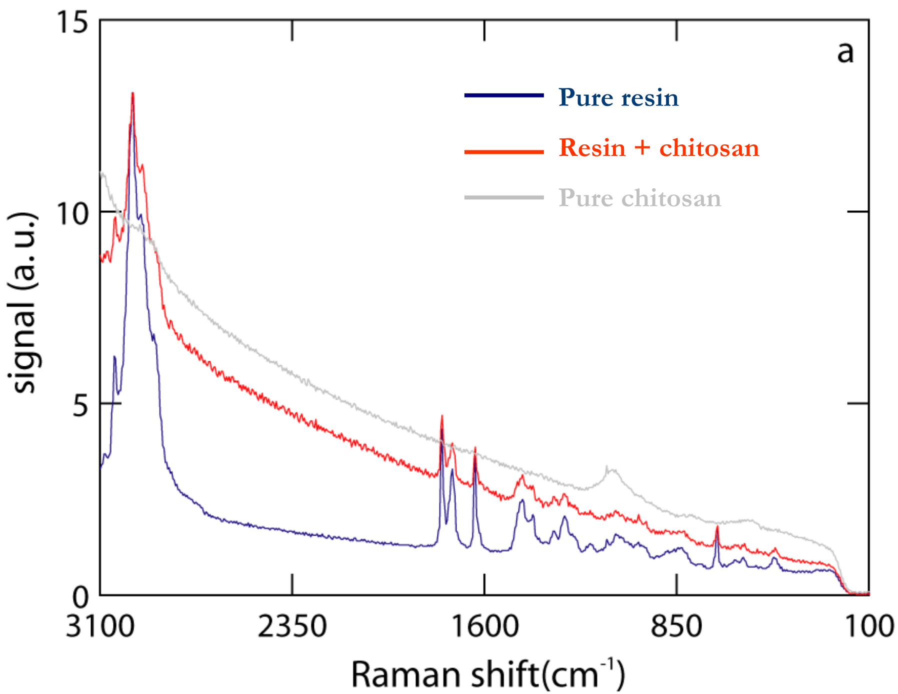
SEM of some fabricated microstructures containing chitosan up to 10% in weight



The microstructures display excellent definition and integrity!

Microstructures containing chitosan

Raman scattering spectrum of films



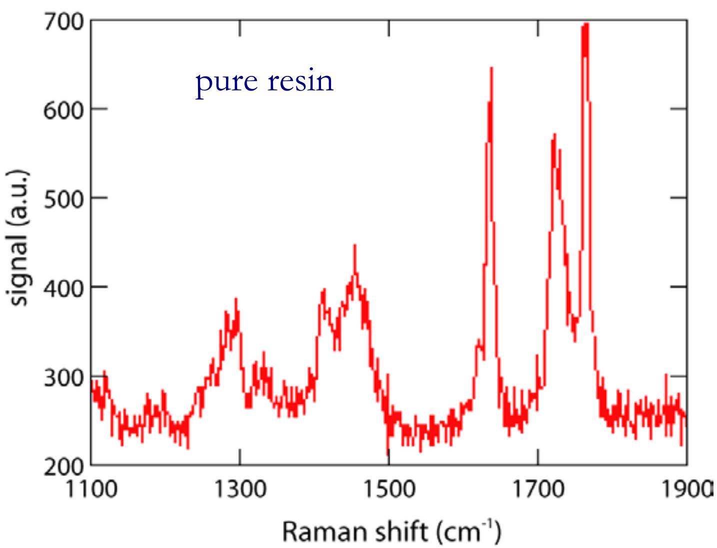
$$\lambda_{exc} = 514\ nm$$

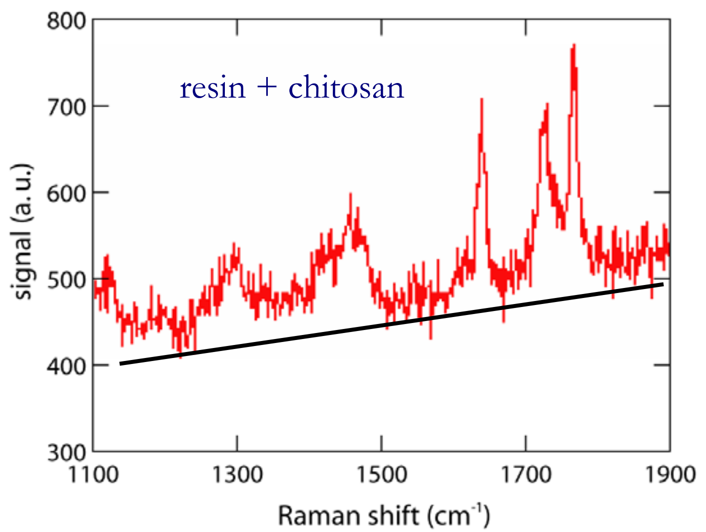
Raman spectrum of films with and without chitosan have a similar shape

Chitosan does not present any distinct Raman signal peak, except an offset signal→ fluorescence

Microstructures containing chitosan

Raman scattering spectrum of microstructures





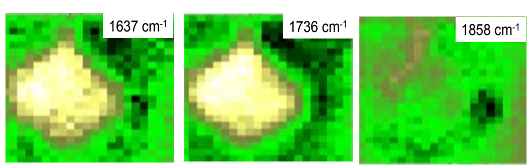
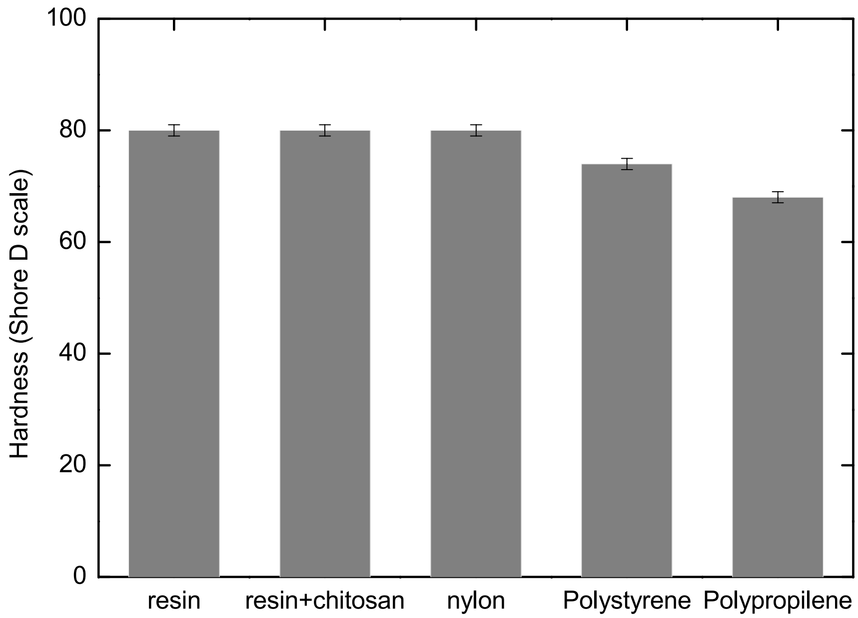


Image obtained by the Raman spectrum signal displays the squared shape of the microstructure

Microstructures containing chitosan

Hardness test using shore D scale



Hardness is higher than PP, PS, and Nylon.

Chitosan does not impair the mechanical properties of the resin.

Both specimen made of pure resin and resin with chitosan present the same hardness value (80±1).

Conclusions

• 3D-microstructures with MEH-PPV and chitosan can be fabricated via 2PA polymerization for photonics and biomedical applications.

• MEH-PPV preserves its luminescent properties when retained into the microstructure.

• We demonstrate waveguiding by 100-μm long structures containing MEH-PPV. Possibility of application of this fabrication process for photonics devices, such as leds, lasers, etc.

• Chitosan was distributed into the microstructure bulk, preserving its chemical and mechanical properties.

• Chitosan does not react chemically and neither impair the mechanical properties of the resin, a desirable feature for medical applications (e.g. tissue engineering and bone reconstruction)

Acknowledgments

FAPESP

CNPq

CePOF
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