The Role of Photo-Initiators in the Inks for Medical 3D Printing

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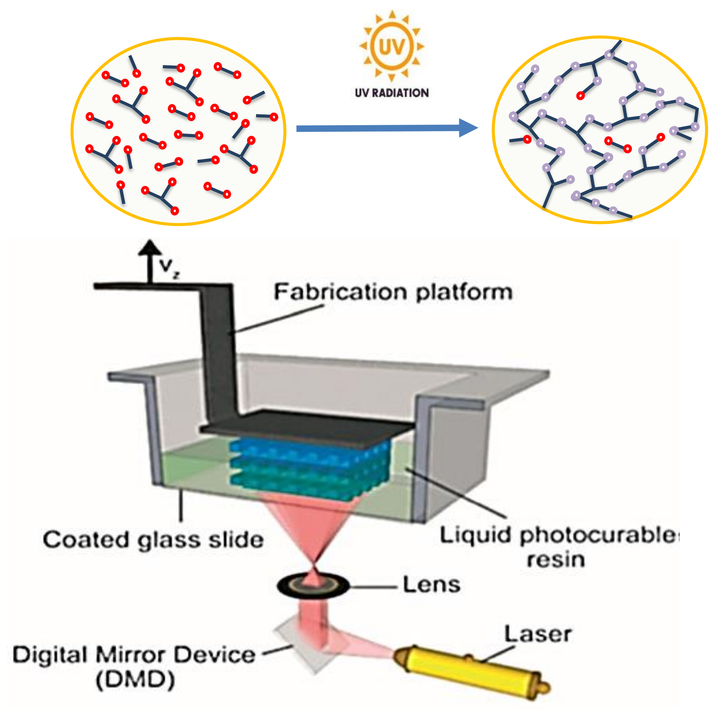
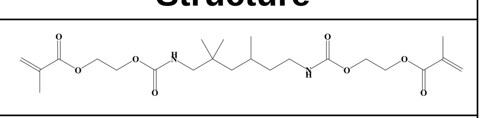
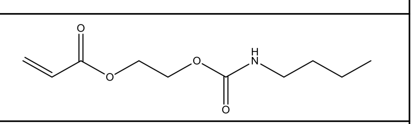
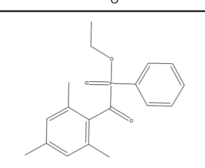
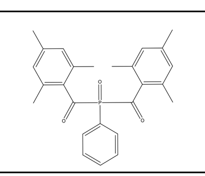


Motivation

Photoinitiators in 3D printing inks are indispensable components for light-based additive manufacturing of medical implants. Due to the recently described genotoxicity of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), we investigate two alternative photoinitiators, namely phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BPO) and ethylphenyl(2,4,6-trimethylbenzoyl)phosphinate (TPOL) on their photo-curing behavior. For this purpose, the photo-curing of urethane acrylate-based formulations containing different amounts of BPO or TPOL (0.1, 0.5, 1.0, 1.5 wt%) was investigated using photo-DSC analysis and a digital light processing (DLP) 3D printer.

Materials

- UrDMA and UrA1 were used as monomers.
- TPOL or BPO was added as photoinitiator.

Compound name	Structure
Diurethane dimethacrylate, a mixture of isomers (**UrDMA4**)	
2-[[(Butylamino)carbonyl]oxy]ethyl acrylate (**UrA1**)	
Ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate (**TPOL**)	
Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (**BPO**)	

UV-Vis Spectroscopy

- TPOL and BPO have maximal absorption at 371 nm and 369 nm, respectively, while UrA1 and UrDMA4 are completely transparent in this region.
- BPO is more photon-reactive than TPOL for the DLP 3D printer (365 nm).

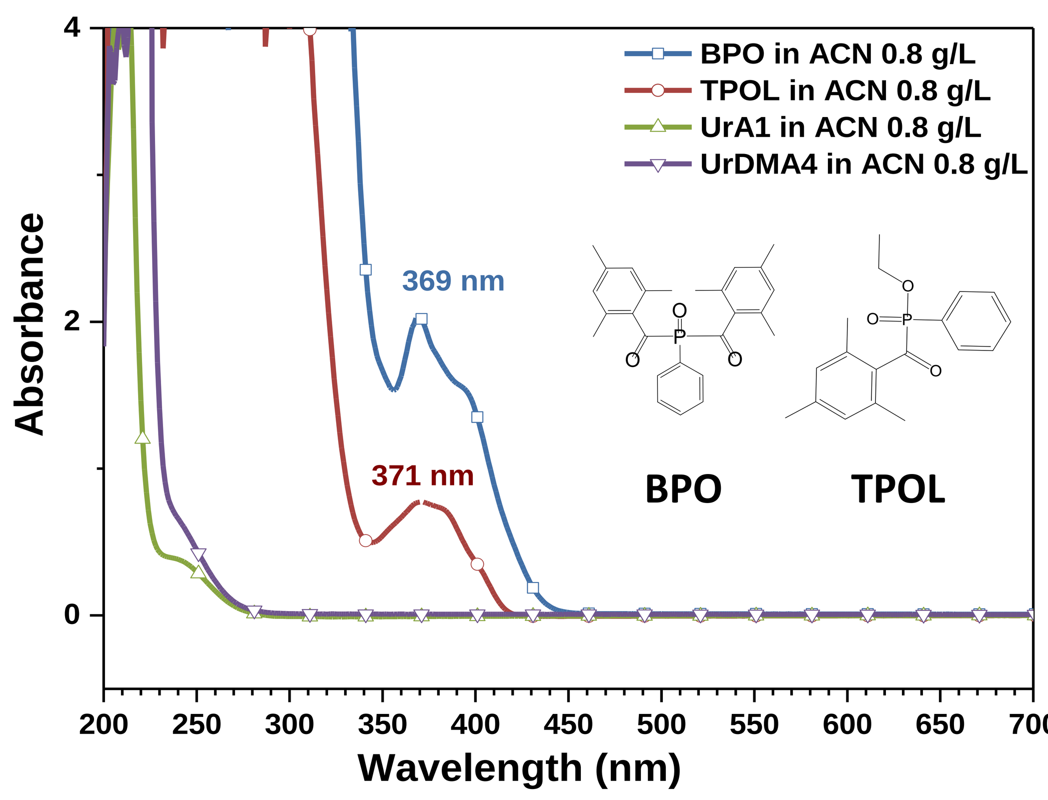
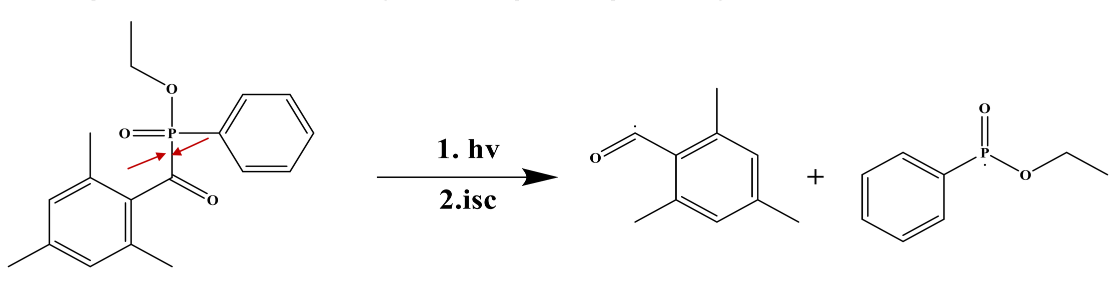
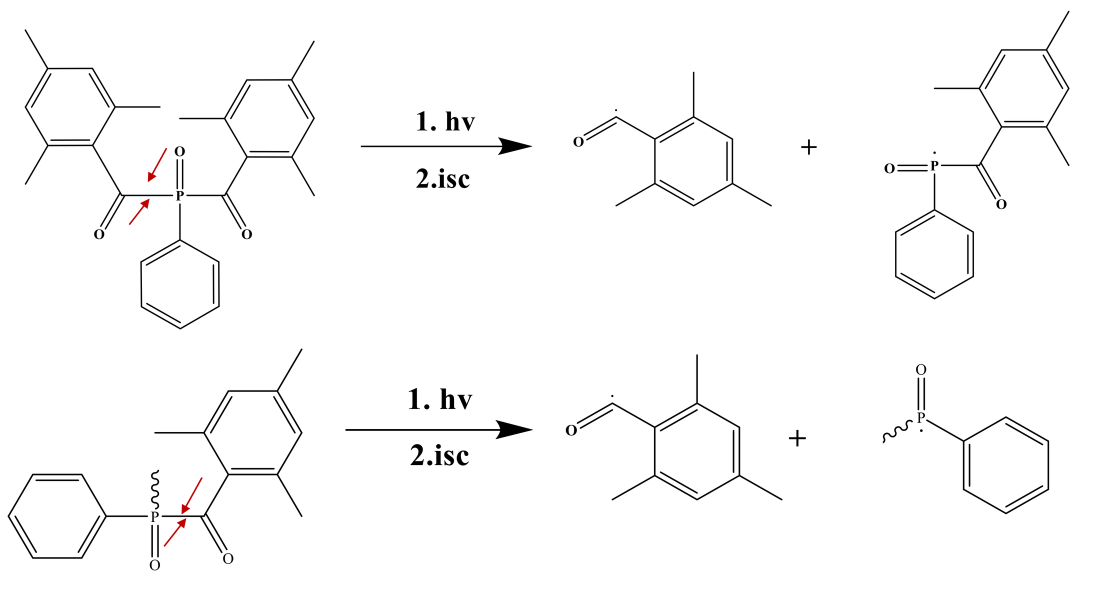


Fig. 1: UV-VIS absorption spectra of BPO, TPOL, UrA1, and UrDMA4.

- Upon irradiation, the α cleavage reaction can occur for TPOL and BPO under triplet-state to produce benzoyl and phosphinoyl radicals.



- BPO is highly effective due to the generation of four radicals. After the addition of the primary radical to the monomers, another second α cleavage reaction occurs.



Kinetics studies of photo-curing

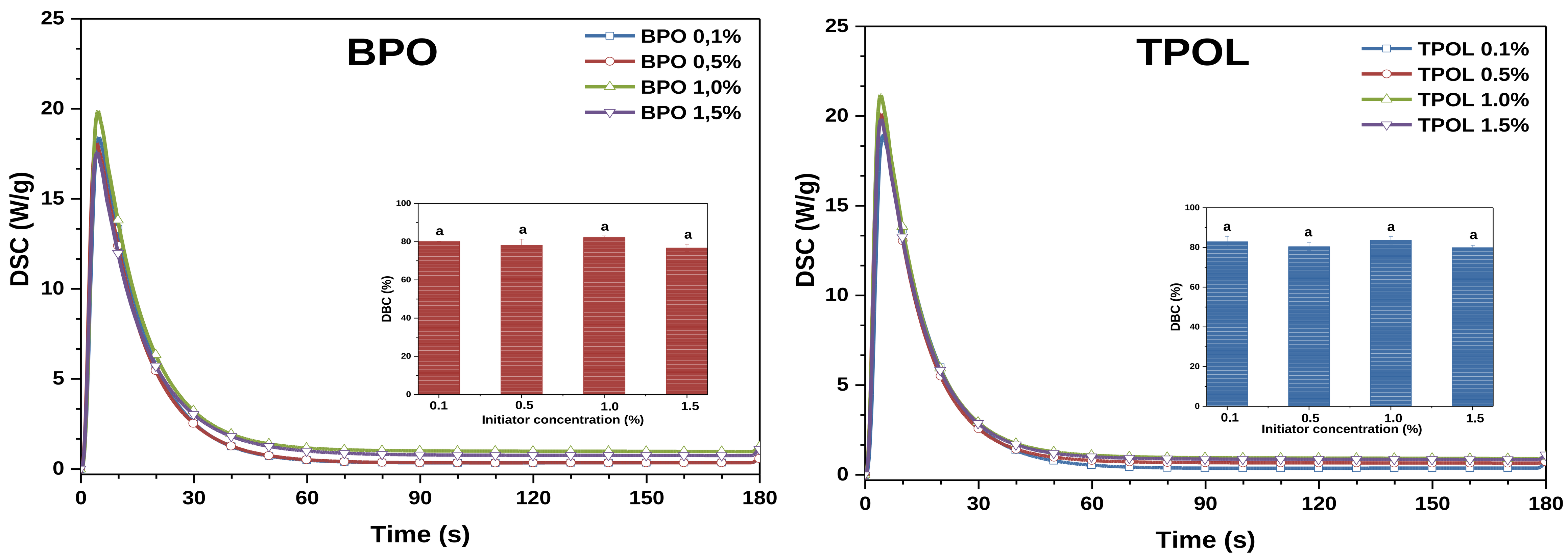
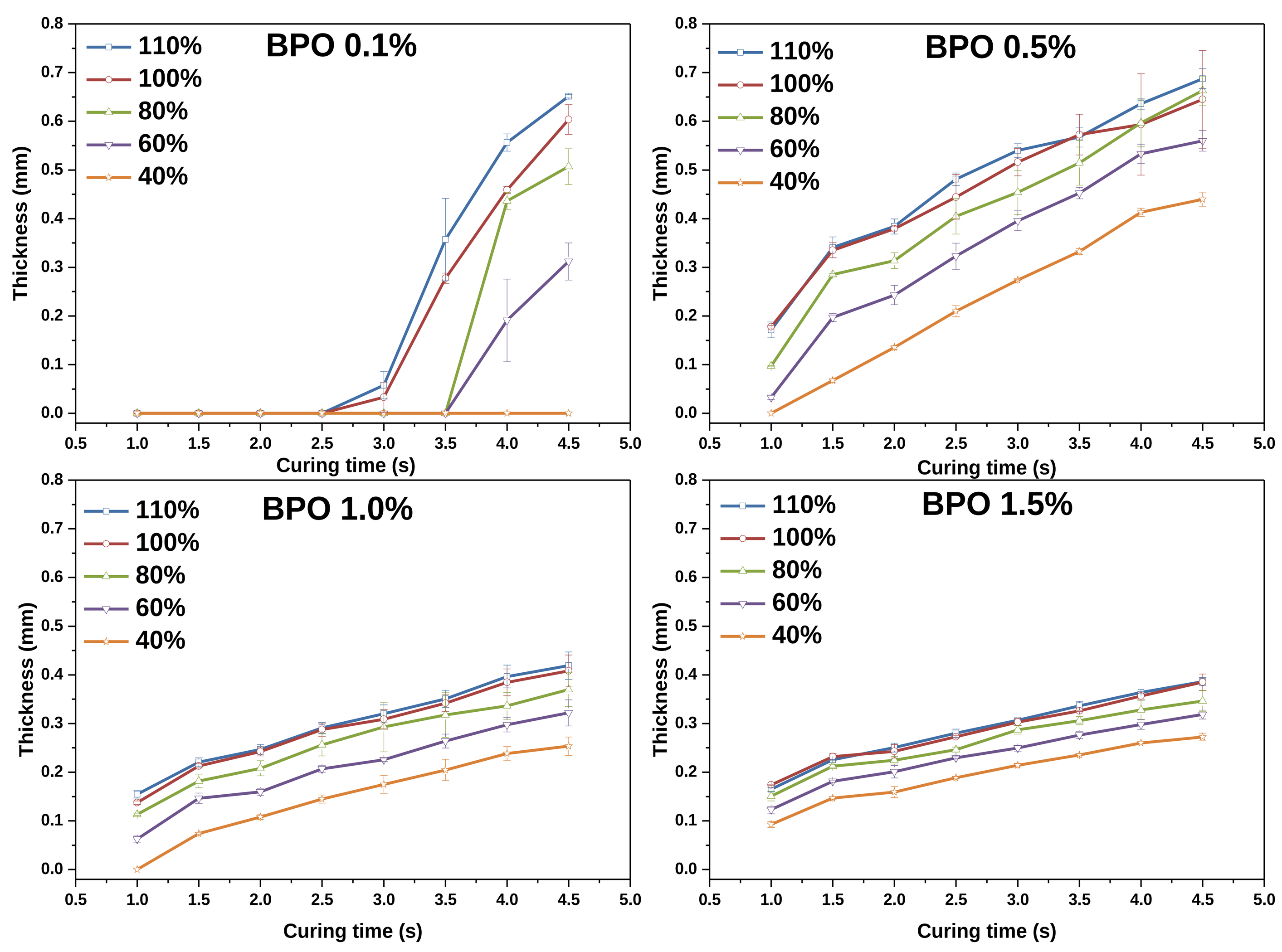


Fig.2. Photo-DSC for the formulations containing different concentrations of BPO or TPOL under N_2 atmosphere at 25°C. The intensity of the UV lamp was 1 W/cm².

- According to the ANOVA and LSD tests for multiple comparisons, the DBC values for the formulations containing different amounts of BPO or TPOL were not significantly different (*p*>0.05).

DLP 3D Printing



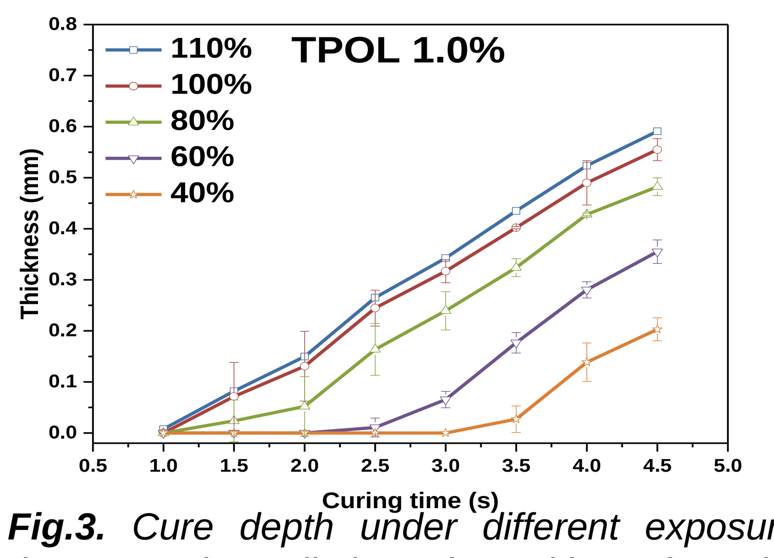
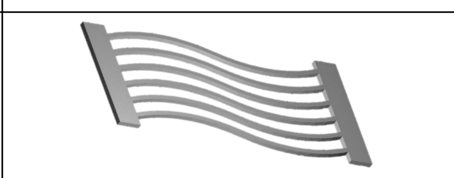
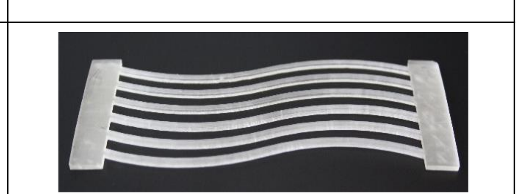
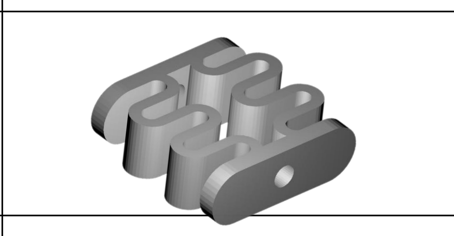
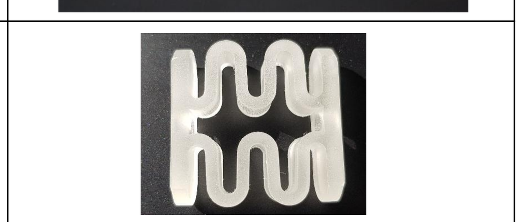
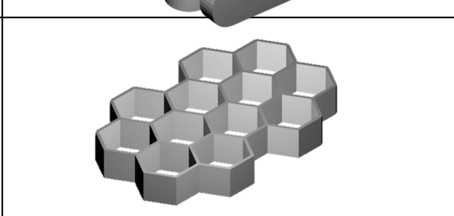
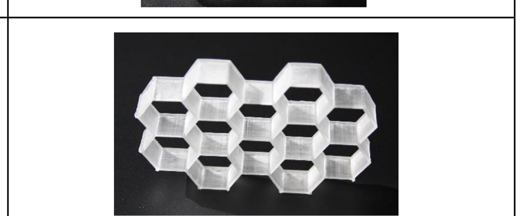
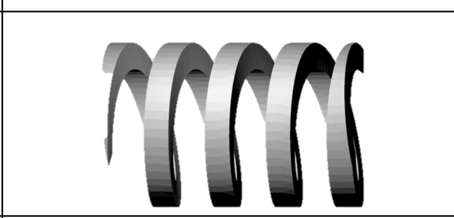
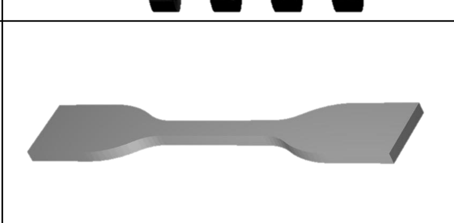
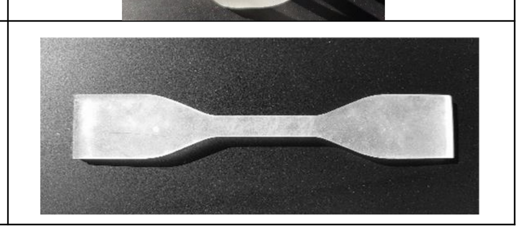


Fig.3. Cure depth under different exposure times and radiation intensities for the formulations with different BPO or TPOL concentrations.

- BPO with high extinction coefficient showed a low light penetration depth.
- Penetration depth was decreased by increasing photoinitiator concentration.
- High penetration depth will cause over-curing of preceding layers.

3D Printed Objects

Samples	CAD models	3D-Printed objects
Wavy fiber		
Ressort		
Hexagonal		
Spring		
Bone-shape specimen		

SEM & Mechanical Characterization

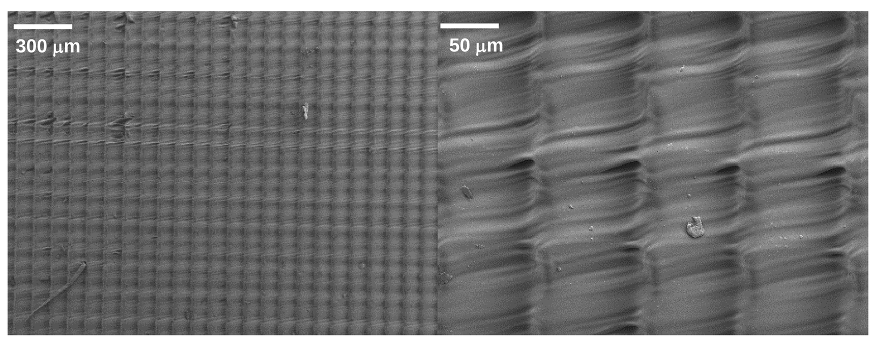
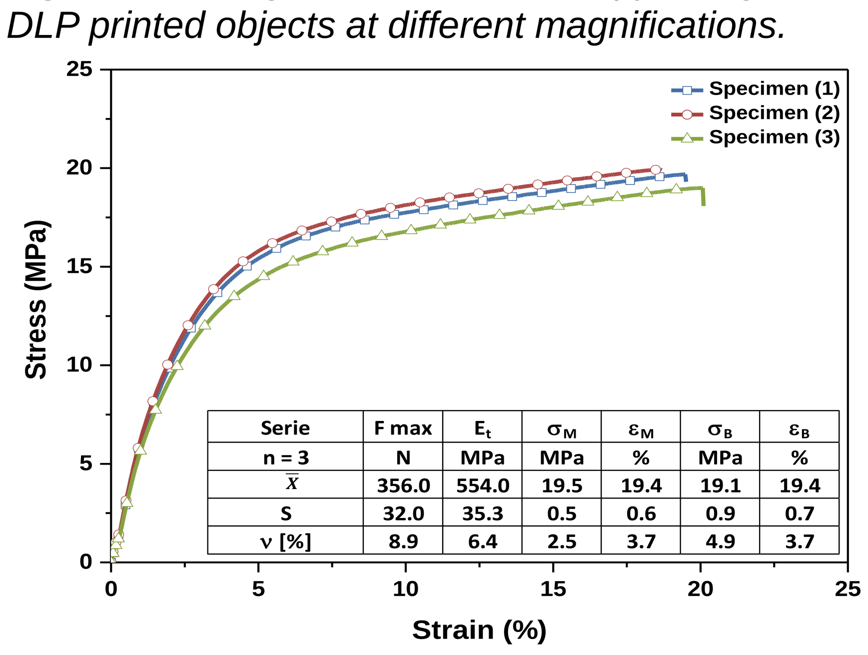


Fig.4. Scanning electron microscopy images of DLP printed objects at different magnifications.



Serie	F max	E_t	σ_M	ε_M	σ_B	ε_B
n = 3	N	MPa	MPa	%	MPa	%
$\bar{x}$	356.0	554.0	19.5	19.4	19.1	19.4
s	32.0	35.3	0.5	0.6	0.9	0.7
ν [%]	8.9	6.4	2.5	3.7	4.9	3.7

Fig.5. Stress-Strain curves and mean mechanical characteristics for 3D printed specimen.