

Supplementary Materials

Photopolymerization of Limonene Dioxide and Vegetable Oils as Biobased 3D-Printing Stereolithographic Formulation

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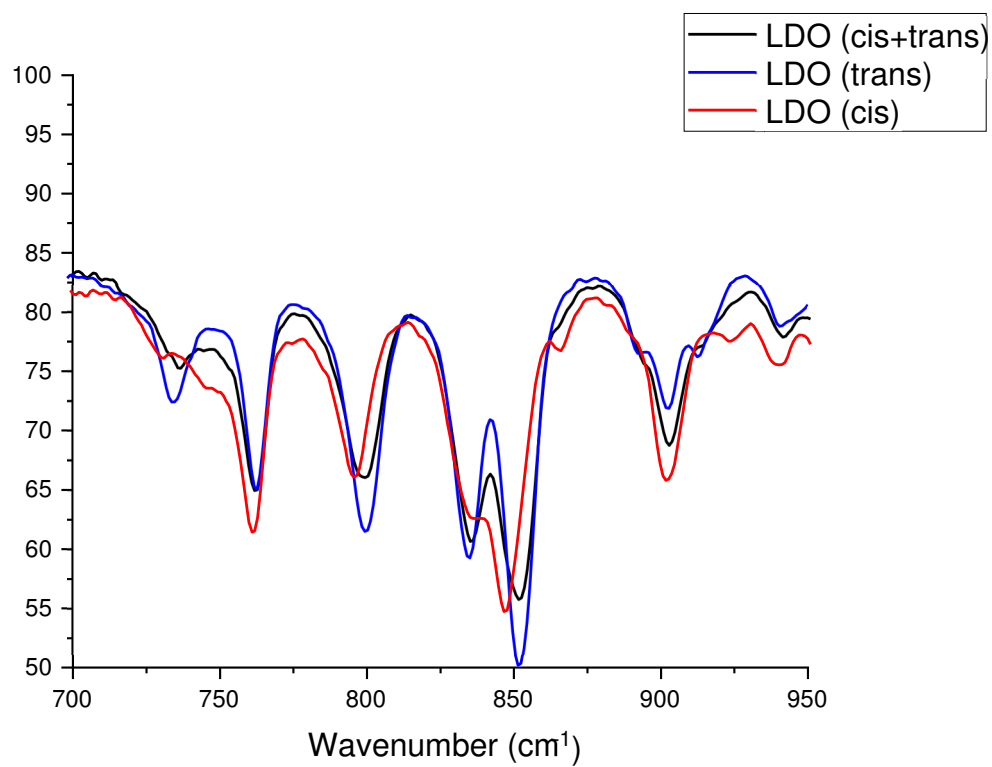


Figure S 1 FTIR spectrum of the LDO/PAG mixture depending on the isomers cis-trans of LDO used (PAG = 0.1 wt%, 1 minute irradiation, 60% relative humidity). The intensities are absolute (no normalization)

In order to compare FTIR spectra in between them, spectra were normalized by the band at 2950 cm^{-1} (see Figure S2). This procedure is justified by the fact that the concentration of C-H bonds remains unchanged during the polymerization. Once normalized, the absolute y scale is arbitrary but samples become comparable to each other.

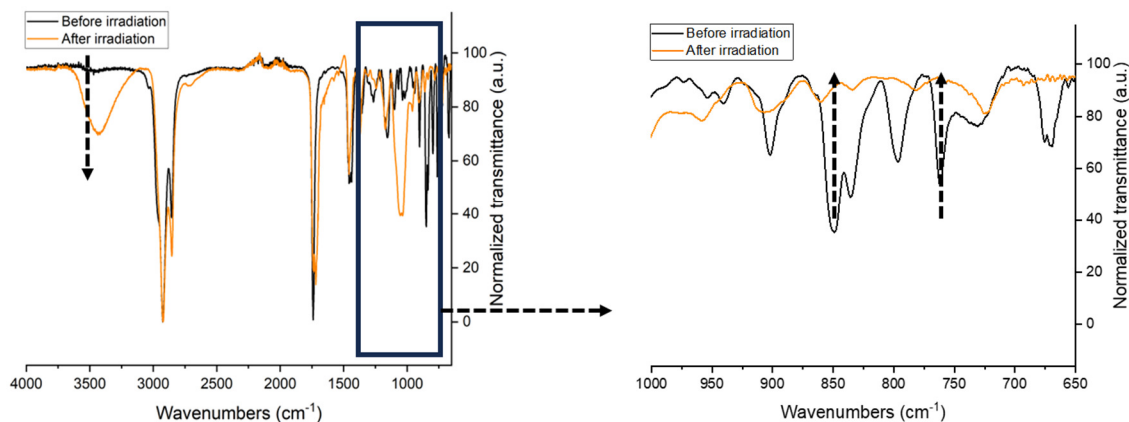


Figure S 2 FTIR spectrum of LDO-ELO (50 wt%) mixture before and after photocationic polymerization (PAG = 1 wt%, 1 minute irradiation, 60% relative humidity). The intensities have been normalized to the band at 2950 cm^{-1} (vertical scale is arbitrary).

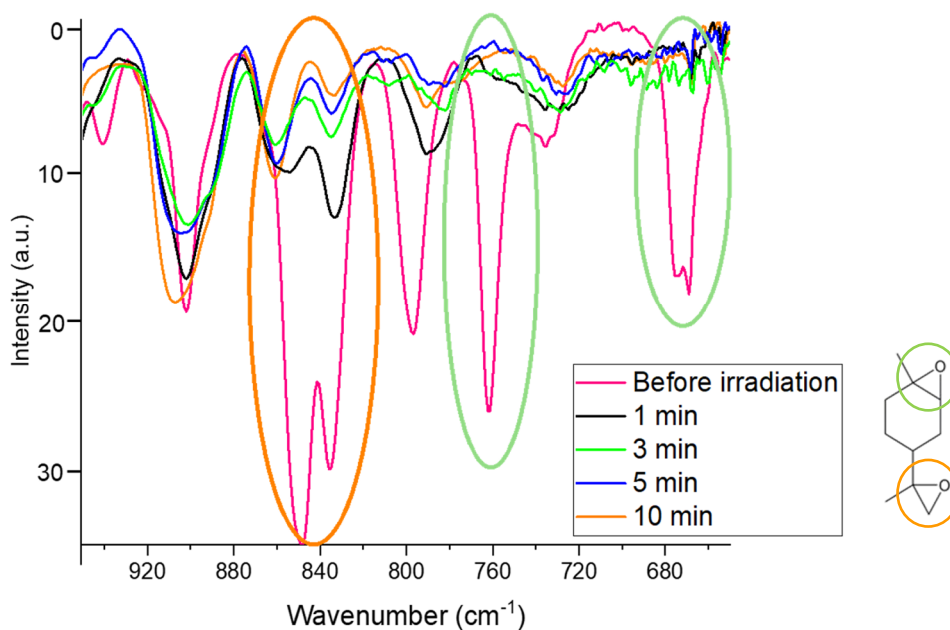


Figure S 3 FTIR spectrum of LDO/PAG mixture with variation of the PAG concentration (1 minute irradiation, 60% relative humidity). The intensities have been normalized to the band at 2950 cm^{-1} (vertical scale is arbitrary).



Figure S 4 Sample of LDO/PAG mixture in an aluminum dish, polymerized at ambient temperature (PAG = 0.1 wt%, 1 minute irradiation, 60% relative humidity).

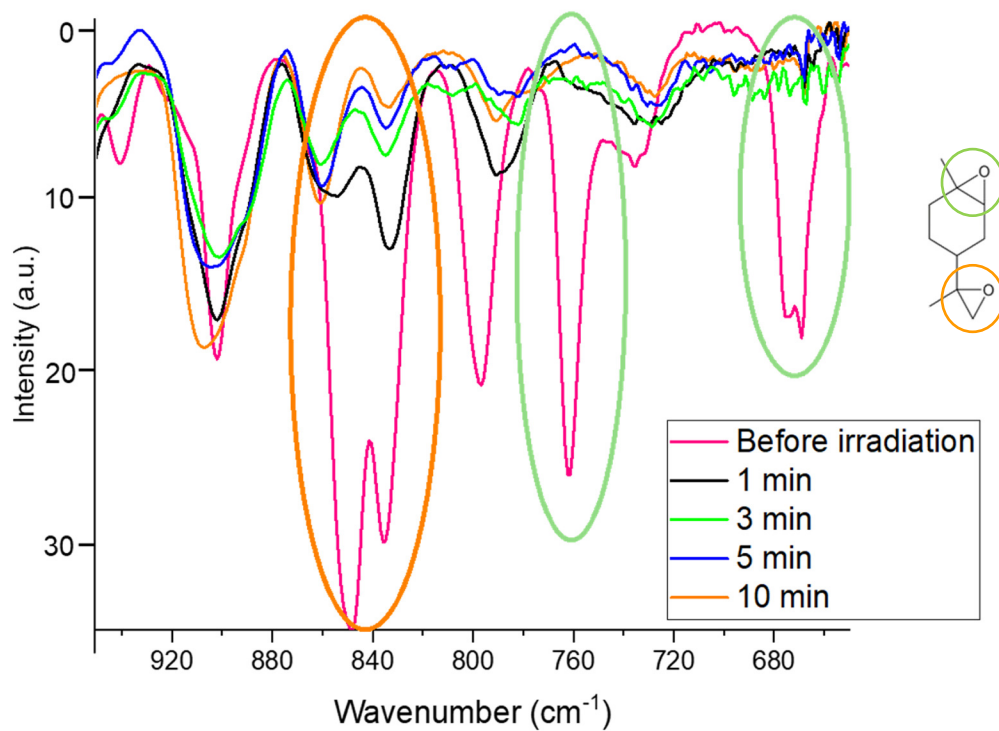


Figure S 5 FTIR spectrum of LDO/PAG mixture with variation of irradiation time (PAG = 0.1 wt%, 60% relative humidity). The intensities have been normalized to the band at 2950 cm^{-1} (vertical scale is arbitrary).

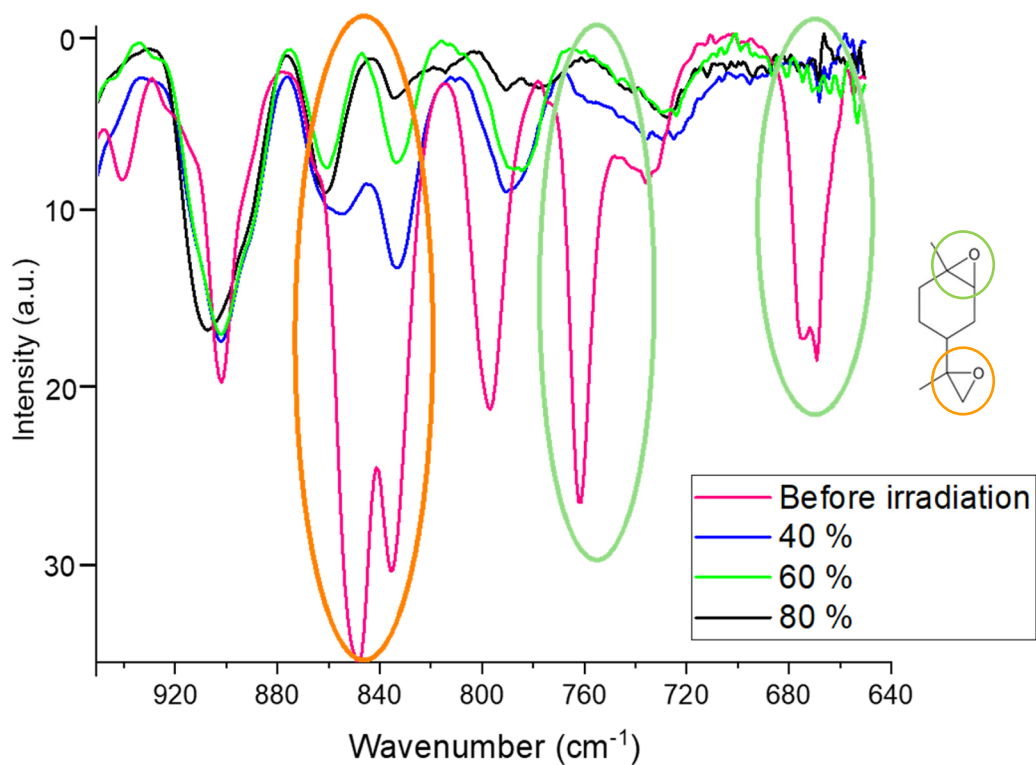


Figure S 6 FTIR spectrum of LDO/PAG mixture with variation of humidity (PAG = 0.1 wt%, 1 minute irradiation). The intensities have been normalized to the band at 2950 cm^{-1} (vertical scale is arbitrary).

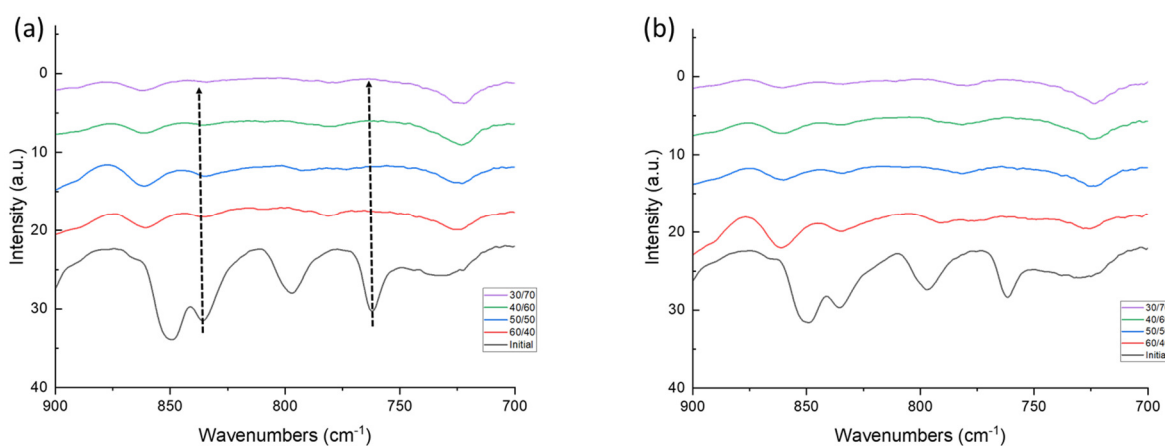
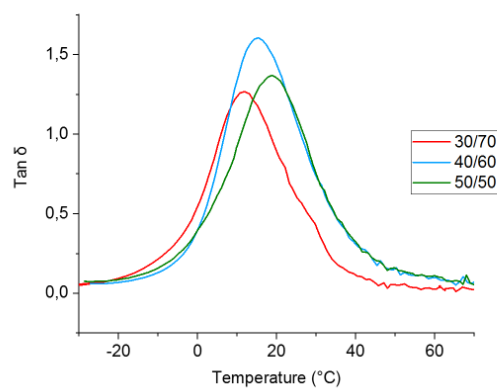


Figure S 7 FTIR spectrum of (a) LDO/ESO and (b) LDO/ELO mixtures at different concentrations (%wt) before and after photocationic polymerization (PAG = 1 wt%, 1 minute irradiation, 60% relative humidity). The intensities have been normalized to the band at 2950 cm^{-1} (vertical scale is arbitrary). Note that the spectra have been vertically offset for the sake of clarity.

Table S 1 Storage modulus, loss modulus, at different temperature, by DMTA for LDO/ESO and LDO/ELO mixtures at different concentration (%wt) after photocationic polymerization (PAG = 1 wt%, 1 minute irradiation, 60% relative humidity).

Formulation	-30°C		0°C		25°C	
	Storage modulus (MPa)	Loss modulus (MPa)	Storage modulus (MPa)	Loss modulus (MPa)	Storage modulus (MPa)	Loss modulus (MPa)
LDO/ESO 30/70 (wt%)	1244±20	62±1	176±14	102±1	2±1	2±1
LDO/ESO 40/60 (wt%)	1581±22	94±1	390±21	162±3	3±1	4±1
LDO/ESO 50/50 (wt%)	874±16	65±1	234±16	93±1	4±2	5±1
LDO/ELO 30/70 (wt%)	1070±18	84±2	840±26	87±1	71±13	47±6
LDO/ELO 40/60 (wt%)	1103±12	28±1	793±24	70±1	121±21	74±4
LDO/ELO 50/50 (wt%)	933±15	32±1	754±17	71±1	255±26	114±11

(a)



(b)

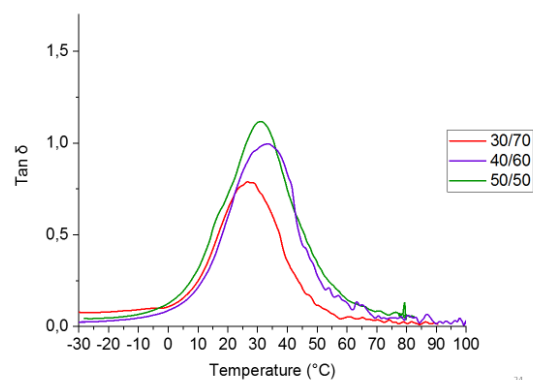


Figure S 8 Tan δ curves by DMTA for the crosslinked epoxy films after photocationic polymerization. (a) LDO/ESO and (b) LDO/ELO mixture (PAG = 1 wt%, 1 minute irradiation, 60% relative humidity).

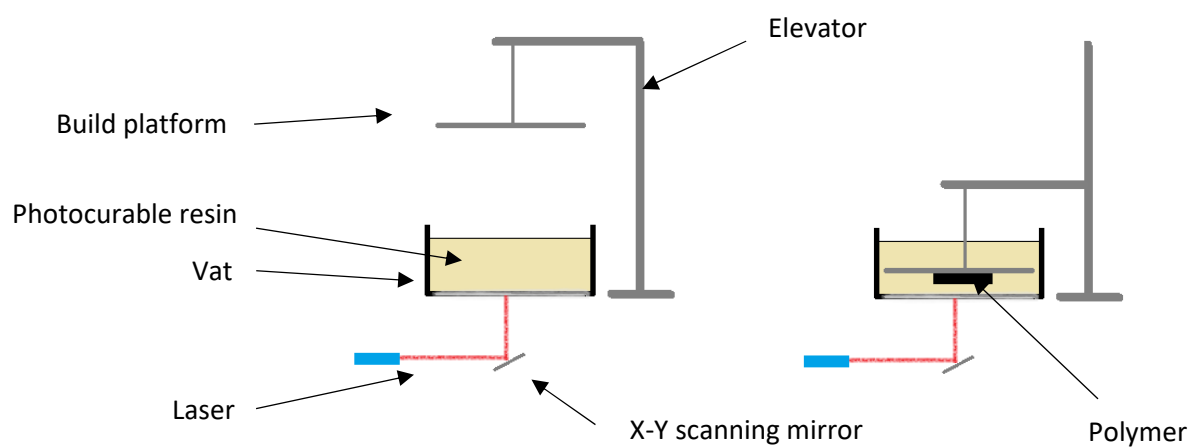
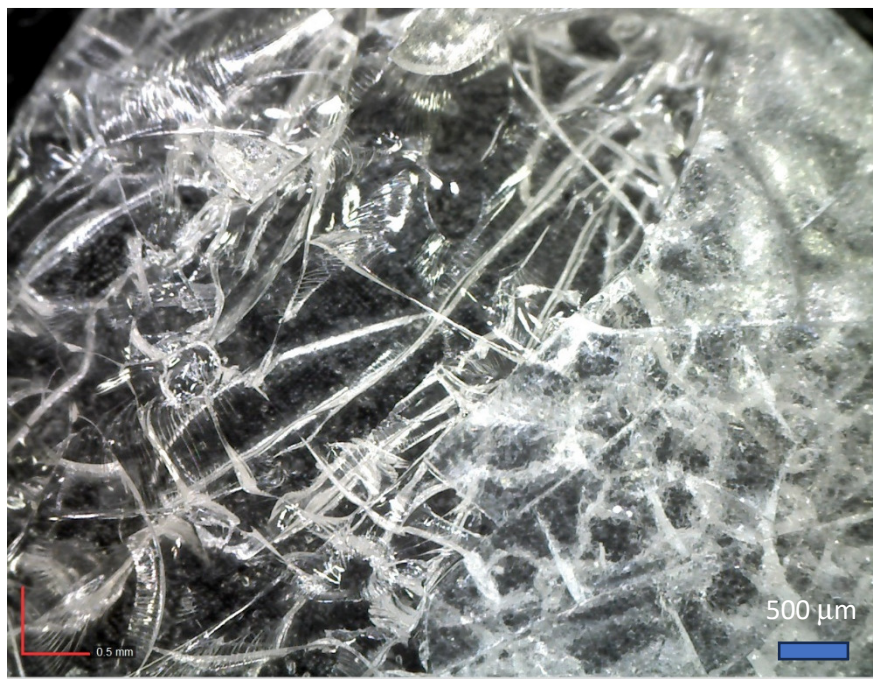


Figure S 9 Schematic principle of stereolithography.

(a)



(b)

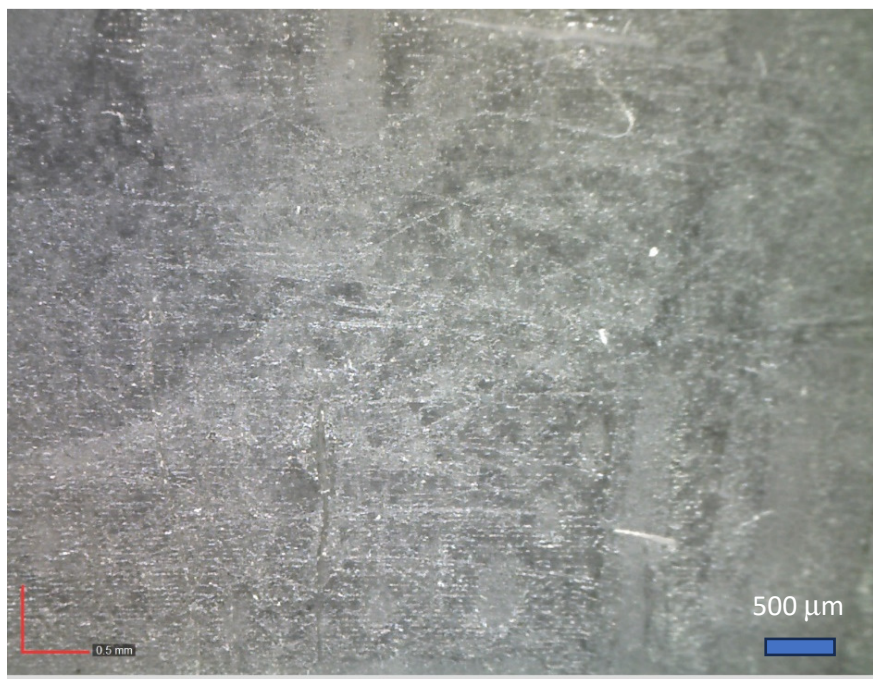


Figure S 10 Picture by optical microscope (DPM 300 from BYK); 3D printed resins LDO/AESO/TMPTA 18/66/16 %wt (0,5%wt of BAPO); (a) without PAG; (b) with 0,5%wt of PAG.

Table S 2 Swelling tests in methanol for the mixture LDO/AESO/TMPTA printed by stereolithography.

LDO/AESO/TMPTA (wt%)	Swelling in MeOH (%)
53/38/9	15.1
31/56/13	10.8
18/66/16	3.6
18/66/16 ¹	2.4

1. curing for 30 minutes at 80°C.

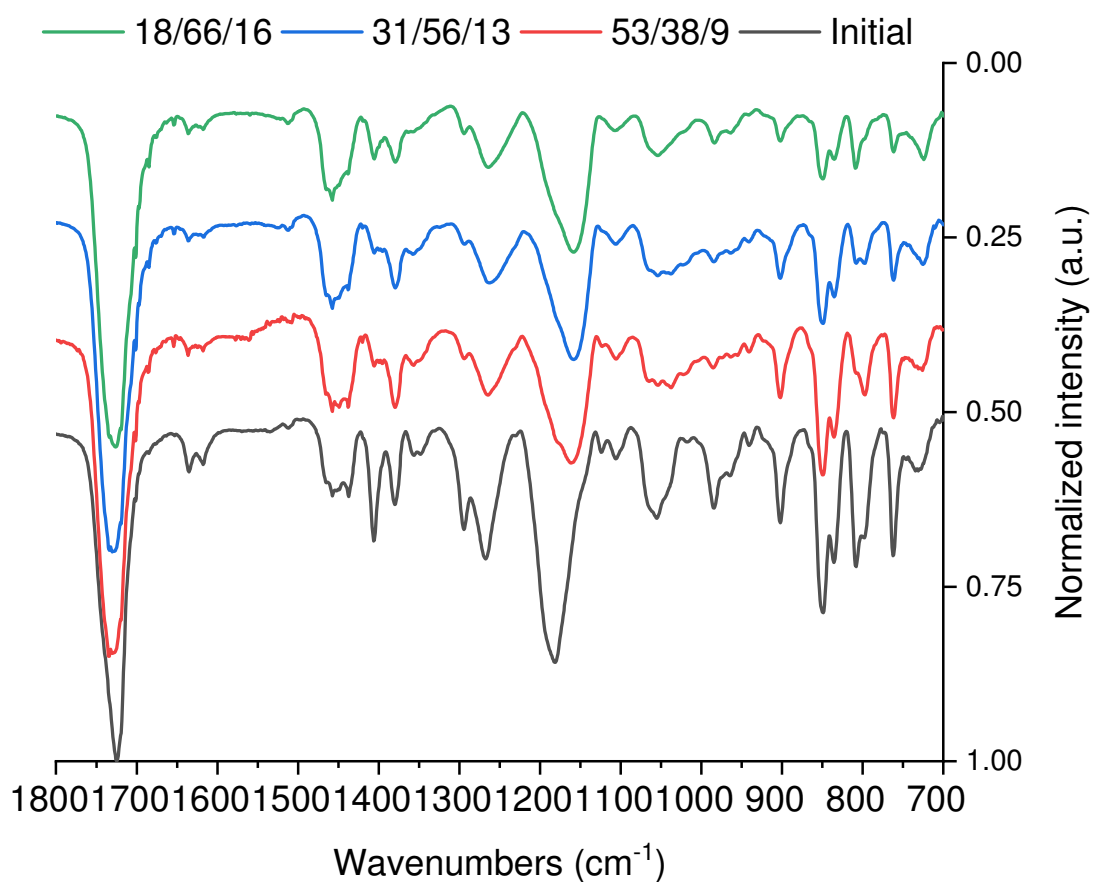


Figure S 11 FTIR spectrum of LDO/AESO/TMPTA mixtures (wt%) before and after 3D printing (0.5 wt% BAPO, 0.5 wt% PAG). The intensities have been normalized to the band at 2950 cm^{-1} (vertical scale is arbitrary). Note that the spectra have been vertically offset for the sake of clarity.

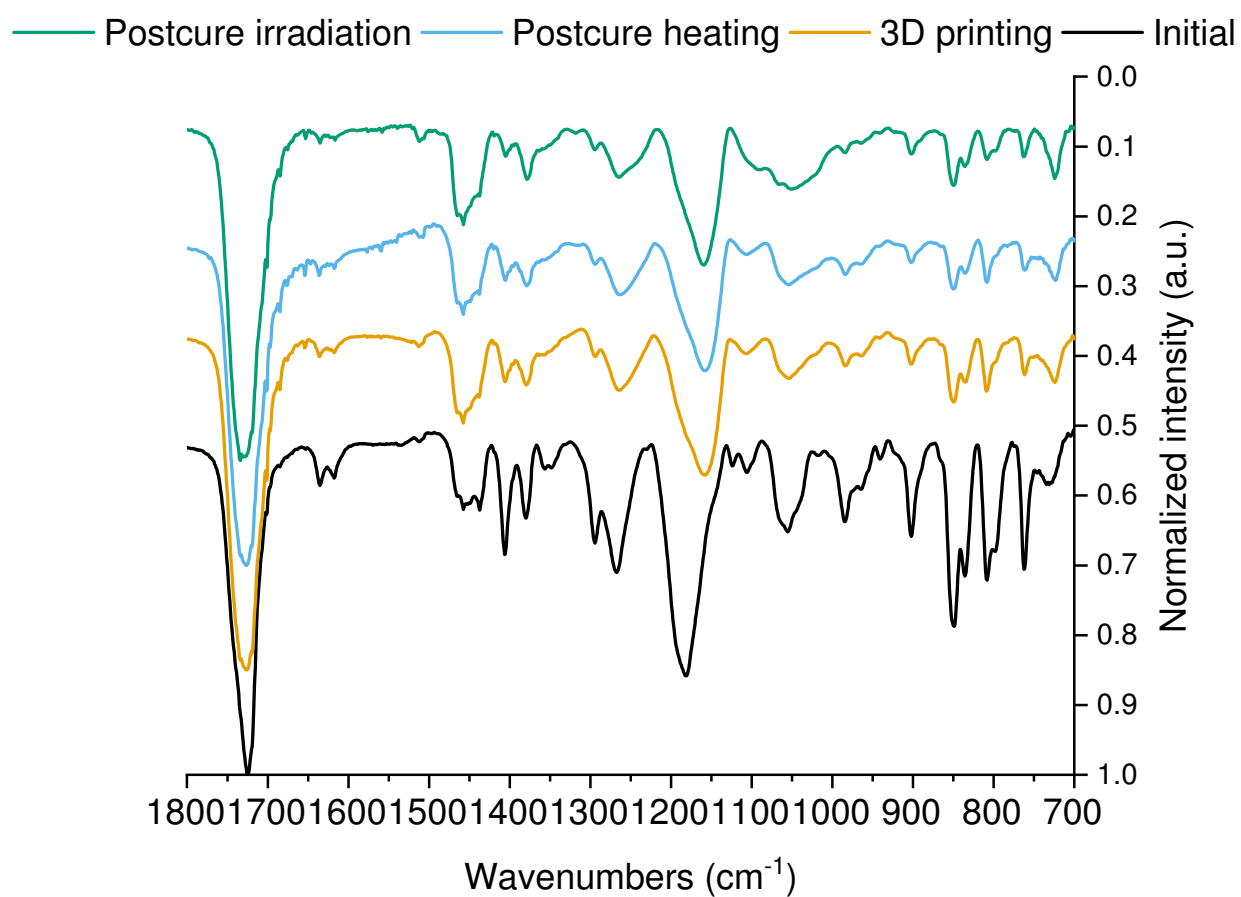


Figure S 12 FTIR spectrum of LDO/AESO/TMPTA mixtures 18/66/16 %wt before 3D printing, after 3D printing, and with a thermal postcure. The intensities have been normalized to the band at 2950 cm^{-1} (vertical scale is arbitrary). Note that the spectra have been vertically offset for the sake of clarity.