Electronic Supplementary Information

Photocurable epoxy-based composite for rapid orthopedic soft casting

Beatrice Tosetto,[a,b,c,] Roberto Mo,[c,] Candido Fabrizio Pirri,[a,c] Ignazio Roppolo[a,c]

a. Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, Turin 10129, Italy.

b. Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di Sotto 8, 06123, Perugia, Italy.

c. Center for Sustainable Future Technologies, Italian Institute of Technology, Via Livorno 60, 10144 Turin, Italy.

Table of content: List of Figures

Table of content: List of Tables

Table S 1. Formulations and curing parameters of samples polymerized with UV light.

PhI		Films		Bulk samples		Single-Layer Composite				Tested with PhS
Name	**phr**	**Light Intensity (mW/cm^2)**	**Irradiation time (s)**	**Light Intensity (mW/cm^2)**	**Irradiation time (s)**	**Light Intensity (mW/cm^2)**	**Irradiation time (s)**	**Polymerization**	**self-standing**	
Iod I	3	130	40	40	120	-	-	Yes, but slow	Yes	Yes
	6	-	-	40	40	30	100	Yes	Yes	Yes
Iod II	6	-	-	40	40	30	100	Yes	No	No
T65	6	-	-	40	40	30	90	Yes	No	No
T67	6.4	40	40	40	40	40	10	Yes, burned	Yes	Yes (but 4.2-2.1 phr)
Solf	4.6	130	30	40	120	20	20	Yes	Yes	Yes (also 6.9 phr)
BTB	5	40	40	40	40	40	40	Yes	Yes	Yes (also 3 phr)

Table S 2. Formulations, curing parameters and results for the evaluation of the different PhI/PhS combination.

Formulation Composition							
PhI		PhS		Irradiation Time[a]		Polymerization	Evaluation[b]
Name	phr	Name	phr	Film	Bulk samples		
Iod I	3	ITX	2	10 min	-	No	E
T67	4.2	ITX	2	9 min	9 min	Incomplete and too slow	E
Solf	4.6	ITX	2	2 min	-	Yes	FA
BTB	5	ITX	2	9 min	9 min	Too slow	E
Iod I	3	C	2	3.5 min	-	Yes, but slow	FA
T67	4.2	C	2	100 s	100 s	Yes	FA
Solf	4.6	C	2	2 min	-	Yes	FA
BTB	5	C	2	100 s	100 s	Yes	FA

[a] With 40 mW/cm^2 visible broad band white light (Hamamatsu lamp)
[b] E: Excluded; FA: further analyzed

Table S 3. Conversion Degree evolution of 2.1 T67/2 ITX composites samples over one month.

		#Single_LD		#Single_HD		#Double	
		DI[a]	NI[b]	DI[a]	NI[b]	DI[a]	NI[b]
CD[c] (%) after:	**1 hour**	77	66	96	88	66	50
	6 hours	82	77	--	--	94	83
	3 days	87	87	--	--	--	83
	7 days	88	--	95	91	95	87
	1 month	89	89	100	97	94	88

[a] Directly irradiated side
[b] Not irradiated (opposite side to the irradiated one
[c] Samples described in Table 2

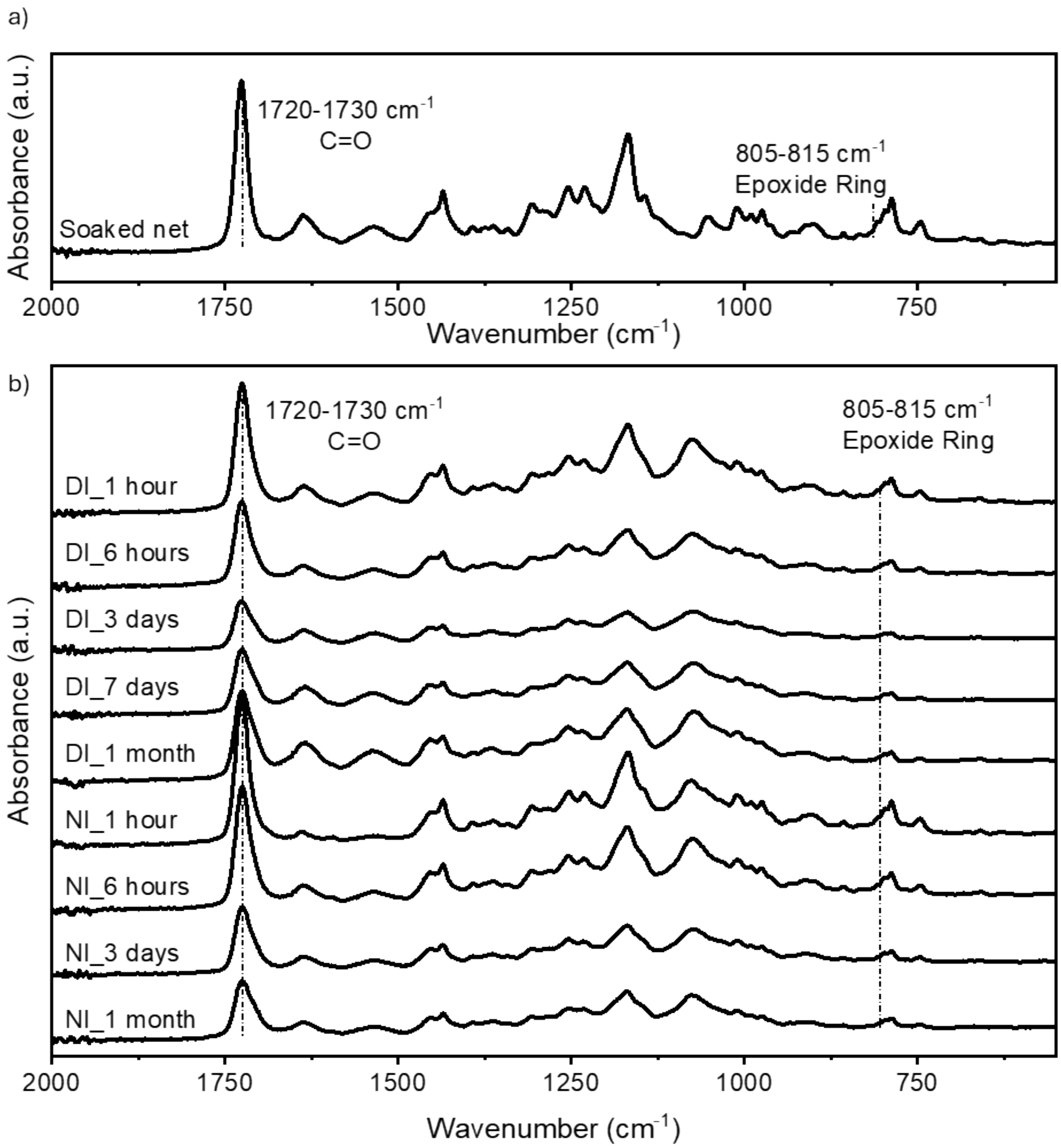


Figure S 1. ATR analyses results of: a) the net soaked in 2.1 T67/ 2 ITX formulation; b) #Single_LD sample

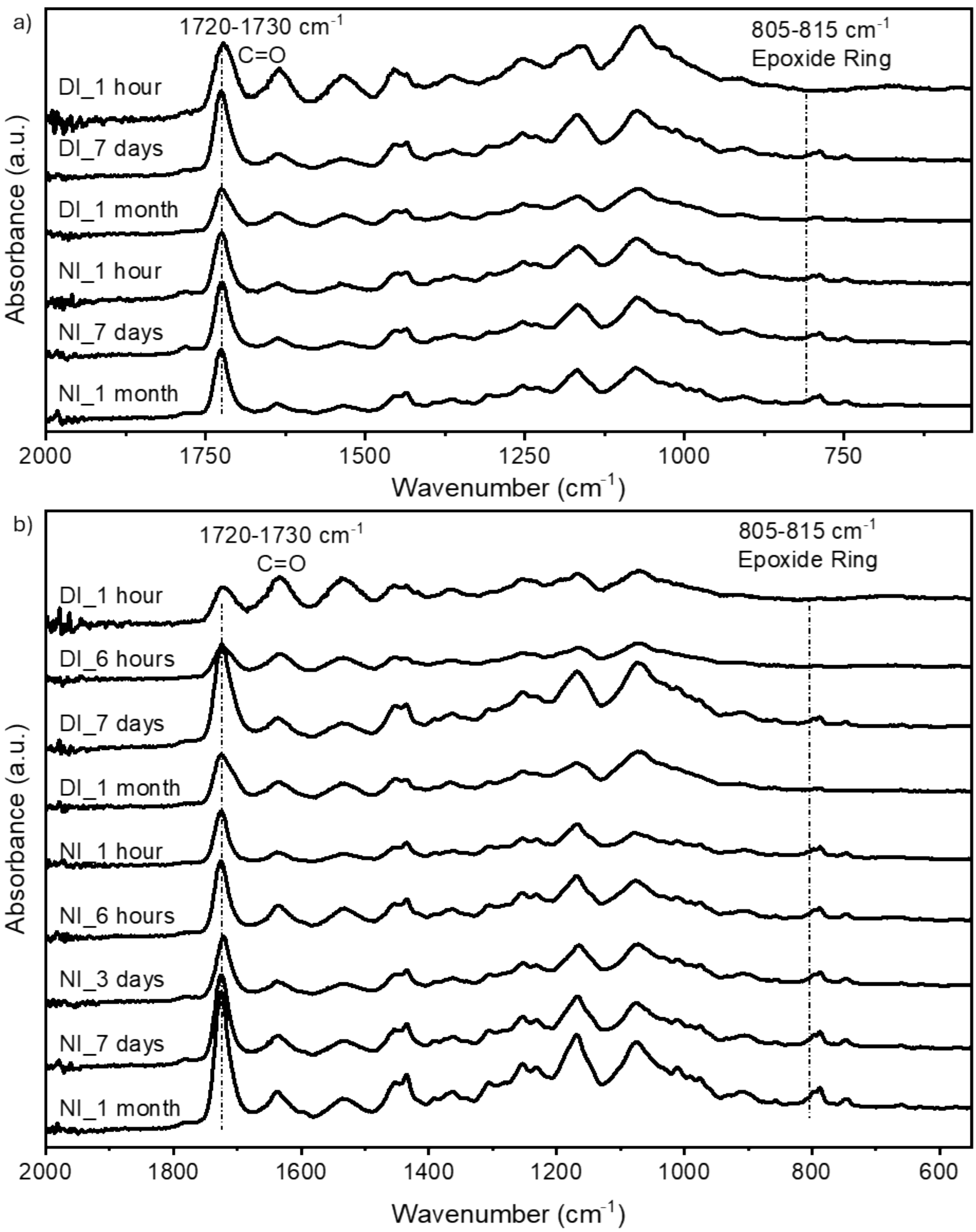


Figure S 2. ATR analyses results of: a) #Single_HD sample; b) #Double sample

Table S 4. Optimized curing parameters for 2.1 T67/2 ITX single- and double- layer composites with broad band visible light.

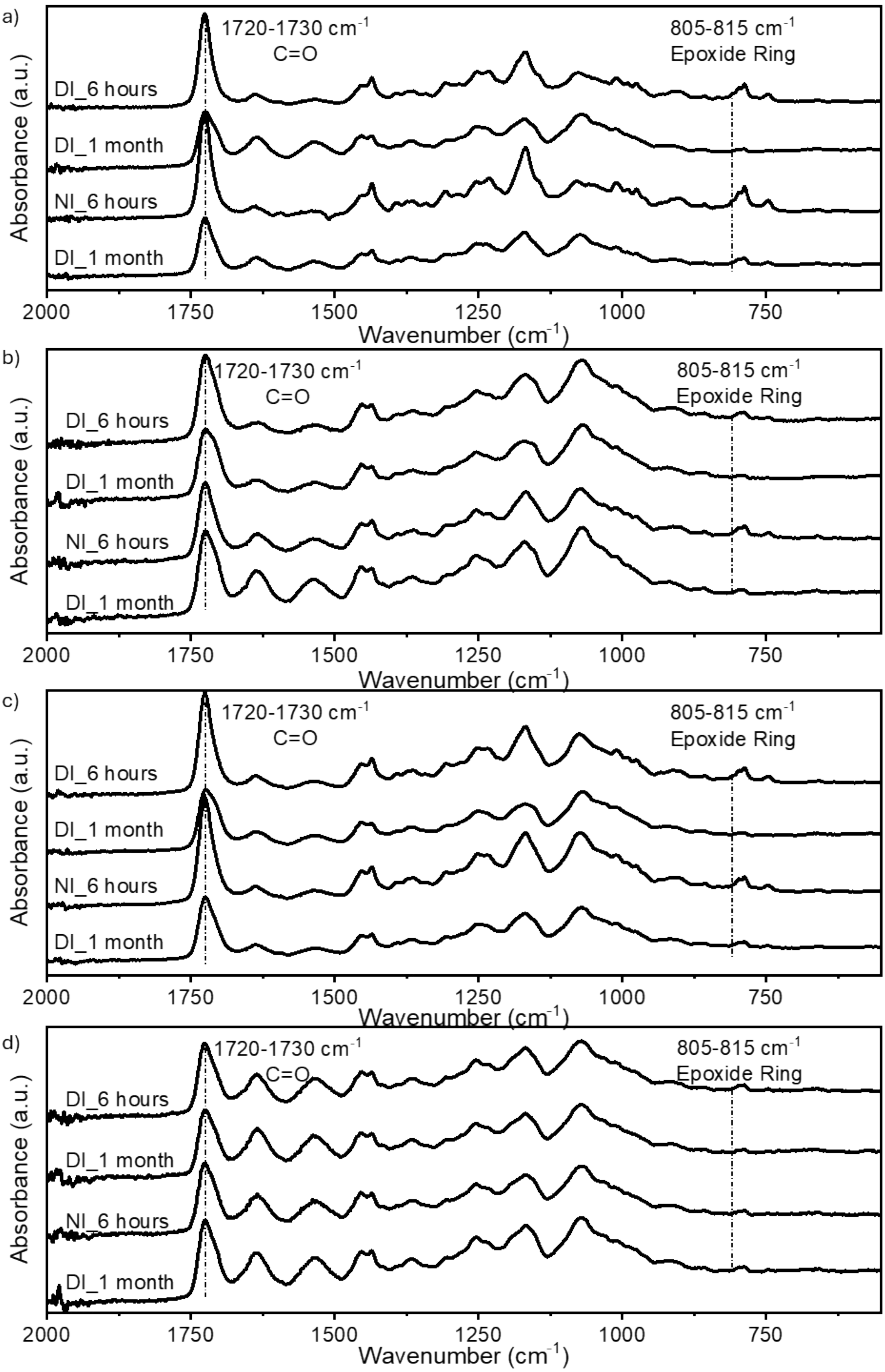
Light source	**Single-layer**		**Double-layer**	
	Light intensity/power	**Irradiation time**	**Light intensity /power**	**Irradiation time**
Solar Simulator	520 W	6 min	520 W	10 min
Hamamatsu Lamp	130 mW/cm^2	50 s	130 mW/cm^2	180 s

Table S 5. One month Conversion Degree evolution of 2.1 T67/2 ITX composites samples polymerized through different broad band visible light. (Spectra are reported in Figure S 1, Figure S 2 and Figure S 3)

Light source	**Layer number**	**Curing condition**	**CD%**			
			DI[a]		**NI**[a]	
			6 hours	**1 month**	**6 hours**	**1 month**
			after irradiation		**after irradiation**	
Solar Simulator	Single-layer	520 W | 2 min	78%	98%	71%	92%
		520 W | 6 min	96%	96%	93%	100%
	Double-layer	520 W | 6 min	89%	97%	82%	96%
		520 W | 10 min	96%	97%	86%	95%
Hamamatsu Lamp	Single-layer	40 mW/cm^2 | 50 s	82%	89%	77%	89%
		130 mW/cm^2 | 50 s	96%[b]	97%	88%[b]	100%
	Double-layer	130 mW/cm^2 | 180 s	94%	94%	83%	88%

[a] DI: Directly irradiated side, NI: Not irradiated side (opposite side to the irradiated one.

[b] FT-IR measurements conducted 1 hour after irradiation



a)
1720-1730 cm-1
C=O
805-815 cm-1
Epoxide Ring
DI_6 hours
DI_1 month
NI_6 hours
DI_1 month
Absorbance (a.u.)
2000
1750
1500
1250
1000
750
Wavenumber (cm-1)
b)
1720-1730 cm-1
C=O
805-815 cm-1
Epoxide Ring
DI_6 hours
DI_1 month
NI_6 hours
DI_1 month
Absorbance (a.u.)
Wavenumber (cm-1)
c)
1720-1730 cm-1
C=O
805-815 cm-1
Epoxide Ring
DI_6 hours
DI_1 month
NI_6 hours
DI_1 month
Absorbance (a.u.)
Wavenumber (cm-1)
d)
1720-1730 cm-1
C=O
805-815 cm-1
Epoxide Ring
DI_6 hours
DI_1 month
NI_6 hours
DI_1 month
Absorbance (a.u.)
Wavenumber (cm-1)

Figure S 3. ATR analyses results of samples: a) single-layer | Solar Simulator | 520 W | 2 min; b) single-layer | Solar Simulator | 520 W | 6 min; c) double-layer | Solar Simulator | 520 W | 6 min; d) double -layer | Solar Simulator | 520 W | 10 min

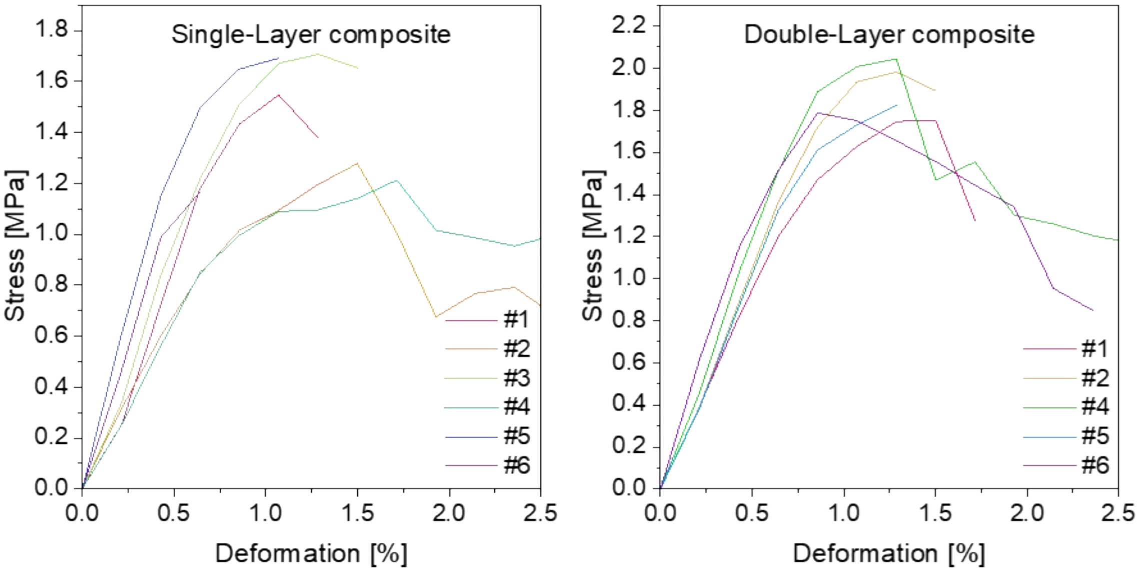


Figure S 4. Stress vs. Deformation curve of 2.1 T67/2 ITX single- and double-layer composites analyzed by tensile tests 12 days after the irradiation through Solar Simulator and optimized curing parameters (Table S 4).

Ad-hoc designed Lamp characteristics and curing parameters optimization

The desired goals for a lamp that can suit the requests for curing rapid orthopedic cast consist of: (i) Visible light source, (ii) flexibility in the reachable light intensity, needed to study the proper curing condition, (iii) high lighting spot (>150cm^2), in order to cure big samples (similar to a real arm cast) quickly, and (iv) portability. The selected LED strips (LS-XC06-S410-SD111, produced by Intelligent LED Solutions), are reported in Fig. S2a. The peak wavelength is between 410-420 nm with a radiance angle of 125°, and they were powered by a volt generator at 24 V. Six of those strips were arranged as depicted in Fig. Sb-c. Thanks to the lamp's flexible design it is possible to tune the light intensity and its distribution by modifying the lamp structure's angle or the LED/LED (d_{LED} and d_0) or LED/Sample (d_c) distance.

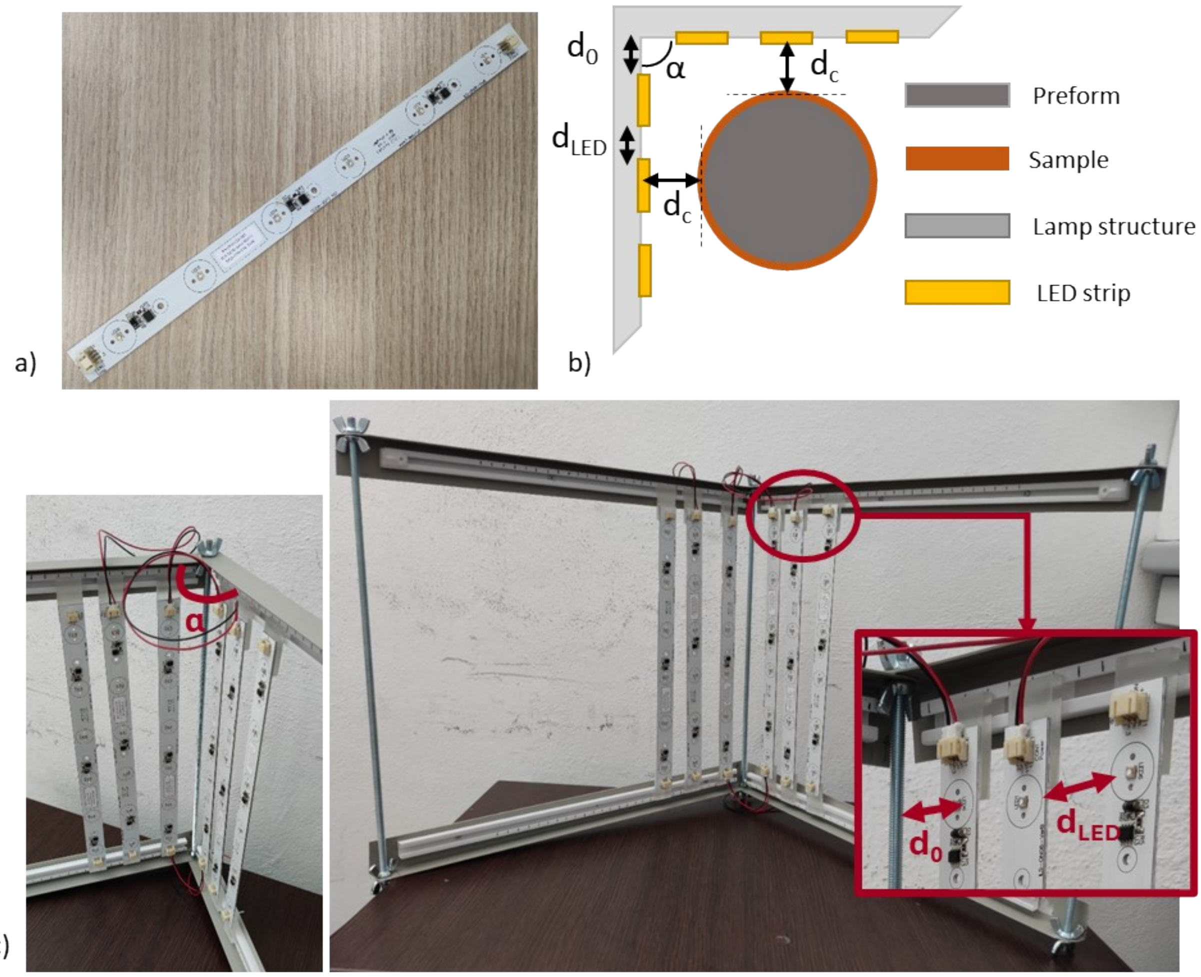


Figure S 5. a) Selected LED strip; Lamp structure's Scheme (top view-b) and Picture (Frontal view-c) highlighting the main geometrical parameter used to tune the light intensity.

The light intensity obtained in three lamp configurations was measured, and results are reported in Tab. S6. Light intensity on the irradiated surface is variable and it has multiple peaks troughs the irradiated area since the LED lamp is composed of 36 LEDs distributed in an area of 440 cm^2.

Table S 6. Geometrical Parameter and measured light intensity of the tested lamp configuration.

Configuration's name	P-1.5	P-3.5	A-3.5
Preform	Flat		Cylindrical
α	180 °		90°
d_{LED}	2 cm		2 cm
d_0	1 cm		3 cm
d_c	1.5 cm	3.5 cm	3.5 cm
Light intensity	1-40 mW/cm^2	5-8 mW/cm^2	5-8 mW/cm^2

The CD correlation with the developed external temperature that was observed with the white broad band light sources was also investigated for the LED lamp, so four tests were performed curing single-layer composites in different curing conditions (curing conditions, CDs, in Tab. S7; developed temperatures in Fig. S3, spectra in Fig. S6). When the light dose was too low (sample S_P-1.5_30), the polymerization process wasn't completely effective, as demonstrated by the low maximum temperature reached (<120°C), and the CD evaluated 6 hours after the irradiation is less than 80%; moreover, the composite appeared to be flexible. Instead, when the light dose is high enough (samples S_P-3.5_40 and S_P-3.5_70): the maximum temperature overcame 180°C, the CD reached a value up to 98%, and stiff spots on the composite were obtained. It is noteworthy that an inhomogeneous rigidity and a strong variability in the CD along the surface were evaluated in those last two samples; this is related to the intrinsic light intensity distribution on the irradiated surface performed by the LED lamp, which results in a non-uniform polymerization, as confirmed by their spotted color (samples' pictures in Fig. S4). In sample S_P-1.5_40, the light color spots match the LEDs position, where the light intensity was higher, and the polymerization was boosted. However, this inhomogeneity problem can be overcome by increasing the light dose, as proven by sample S_P-3.5_90 (curing condition in Tab. S7), which showed a uniform color (Fig. S4) and rigidity. And for this reason, in order to evaluate the proper curing parameters, the samples' color observation was added to the protocol. So, the optimal parameters for curing single-layer composites (Tab. S9) were selected in a conservative mode to ensure a homogeneous sample color by slightly increasing the light dose used for S_P-3.5_70 sample, where a satisfactory CD was already achieved (CD after 6 hours higher than 85-90%). Those parameters were used for sample S_P-3.5_90 and external temperature monitoring, reported in Fig. S5, confirmed the high reaction activation. Instead, for double-layer composites, the optimized parameters (Tab. S9) were selected based on the Temperature-CD analogy that was also confirmed with the LED lamp; in particular, the temperature developed by sample irradiated for 210 s (lamp configuration: P-3.5, irradiation time: 210 s, Fig. S5) matches the ones obtained with proper curing conditions with visible broad band white light (Fig. 2b), while sample irradiated for only 90 s (lamp configuration: P-3.5, irradiation time: 90 s, Fig. S5) didn't reach those values, so the higher energy dose employed should be adequate; moreover this last composites appear to have a uniform color and uniform and high rigidity.

Unfortunately, external temperature monitoring can't emphasize the polymerization dispersion on the surface because it only follows the maximum temperature developed in the framed area; still, a multi-peak trend could be observed in Fig. S3 and Fig. S5, which is related to the polymerization rate dispersion that is an effect of the light intensity distribution.

Finally, a comparison between the external temperature monitoring results obtained with the LED lamp (Fig. S5) and the visible broad band white light (Fig. S2b) was conducted; and the different sample's heating performed by the light sources is evident: with the visible broadband white light, the composites cool down very slowly after the temperature peak when the light is on, and the temperature drastically drop right after the light switch off; instead, LEDs produce less heat, as evidenced by the absence of a strong modification in the temperature as soon as the light went off.

Table S 7. Curing condition and CDs of 2.1 T67/2 ITX single-layer composite samples through LED lamp.

Sample Name	**Curing condition**	**CD[a]**	
		DI-U[b]	**DI-F[c]**
S_P-1.5_30	1-40 mW/cm^2 | 30 s	78%	80%
S_P-1.5_40	1-40 mW/cm^2 | 40 s	93%	86%
S_P-3.5_70	5-8 mW/cm^2 | 70 s	98%	94%
S_P-3.5_90	5-8 mW/cm^2 | 90 s	-	-

[a] FR-IR measurements conducted 6 hours since irradiation
[b] DI-U: Directly irradiated surface under a LED (maximum light intensity,
[c] DI-F: Directly irradiated surface far from a LED (minimum light intensity).

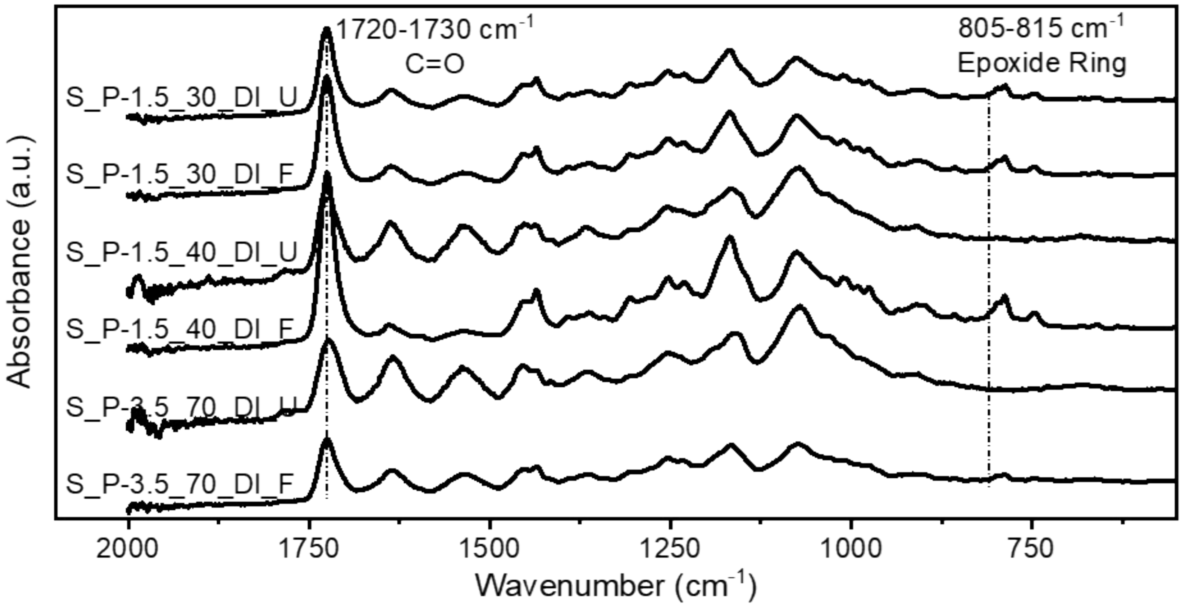


Figure S 6. ATR analyses results of samples reported in Table S 7.

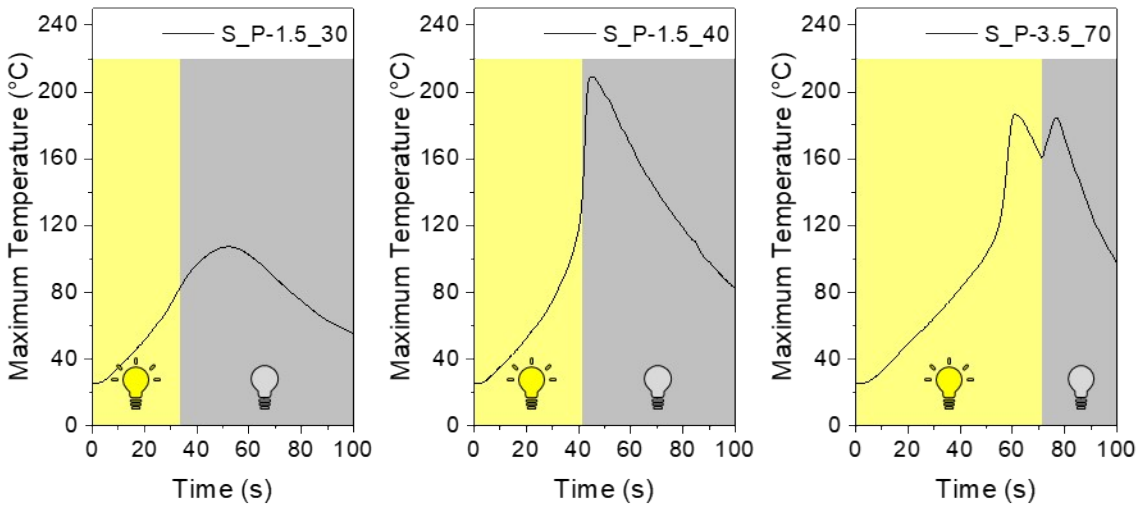


Figure S 7. Evaluation of the temperatures developed on the irradiated side of single-layer composites polymerized in different curing conditions whit LED lamp (sample description and curing parameters in Table S 7).

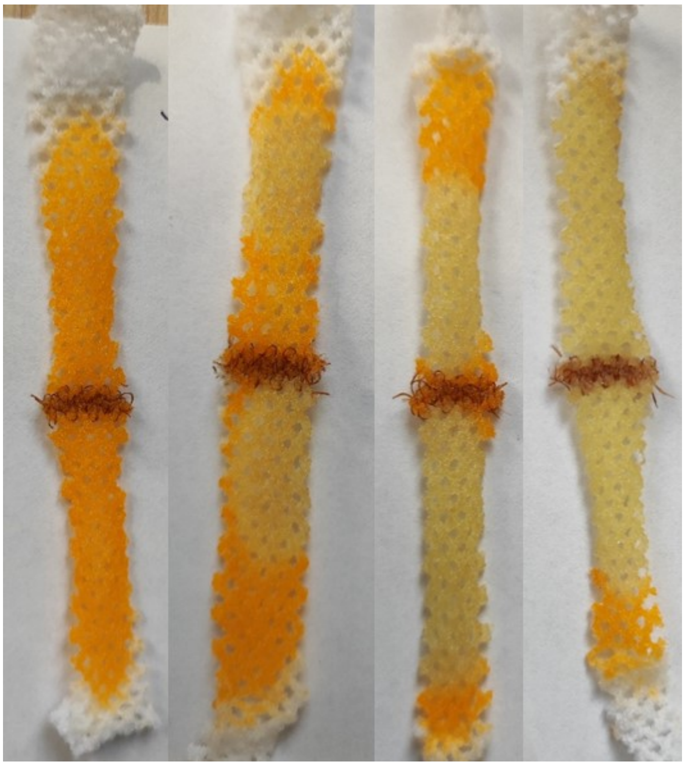


Figure S 8. Picture of single-layer strip samples right after irradiation obtained with the ad-hoc designed lamp: left to right S_P-1.5_30, S_P-1.5_40, S_P-3.5_70, S_P-3.5_90 (sample description and curing parameters in Table S 7

Table S 8. Curing parameters of 2.1 T67/2 ITX samples irradiated with the ad-hoc design LED lamp.

Sample name	n° of Layer (-)	Light Intensity (mW/cm²)	Irradiation time (s)
Single_LED_90s	1	5-8	90
Double_LED_90s	2	5-8	90
Double_LED_210s	2	5-8	210

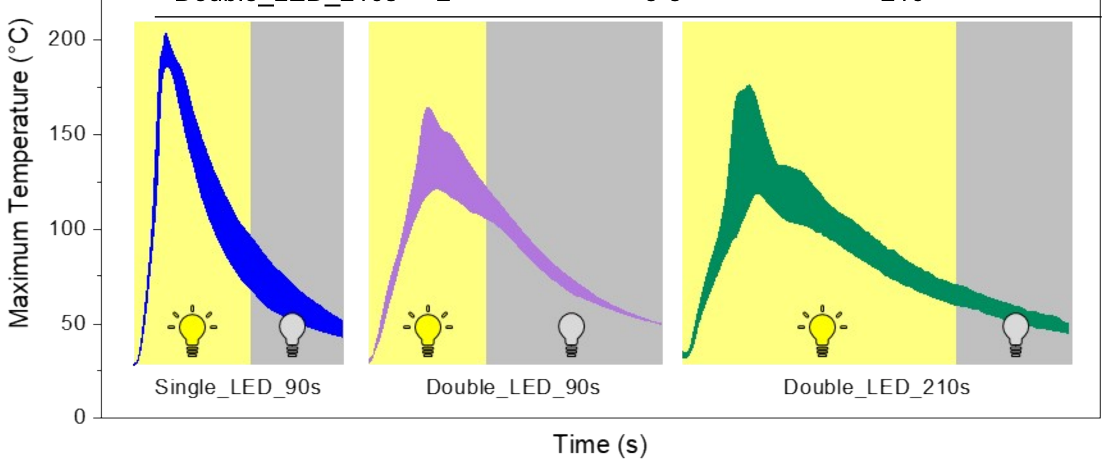


Figure S 9. Maximum temperatures developed on the irradiated side of single- or double-layer composites polymerized in different curing conditions whit LED lamp in one irradiation step (sample description and curing parameters in Table S 8).

Table S 9. Optimized curing parameters for 2.1 T67/2 ITX single- and double- layer composites with the ad-hoc designed LED lamp.

	Single-layer	**Double-layer**
Light intensity	5-8 mW/cm^2	5-8 mW/cm^2
Irradiation time	90 s	210 s

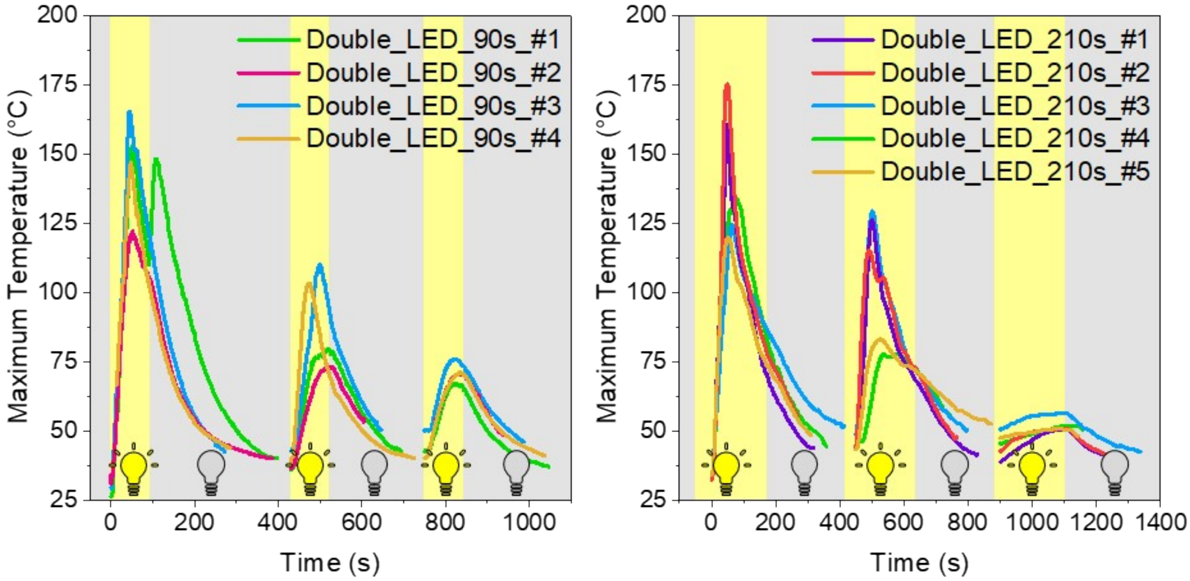


Figure S 10. External maximum temperatures developed on the irradiated side of 2.1 T67/2 ITX cylindrical double-layer composites samples described in Table S 8 and irradiated in 3 steps.

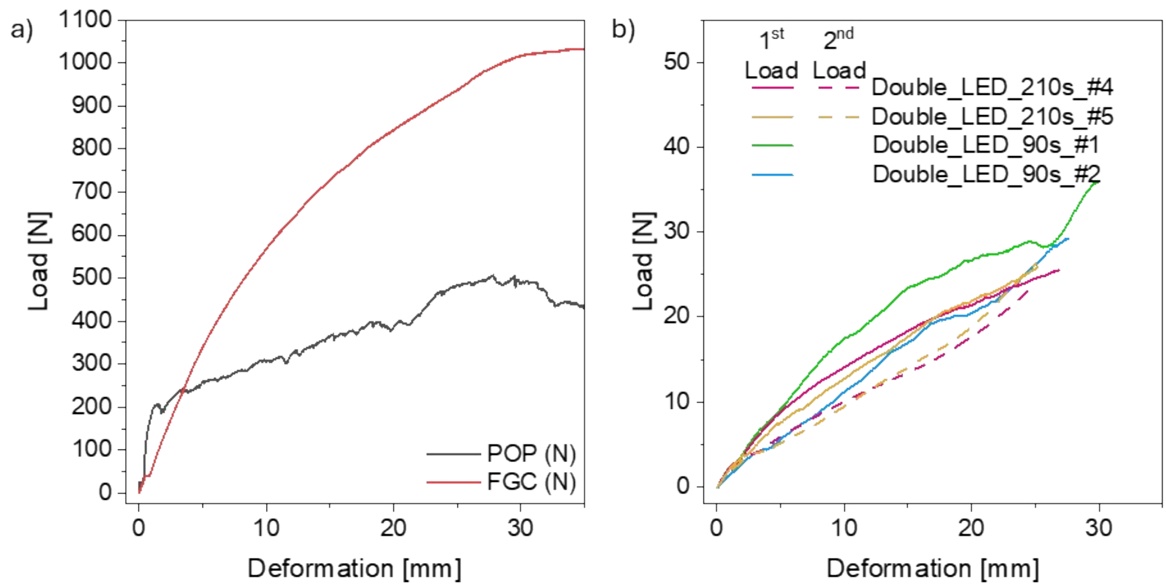


Figure S 11. Load vs. Deformation of: a) POP and FGC samples prepared by a registered technician; b) cylindrical double-layer composites cured with LED Lamp (parameters in Table S 8) in 3 steps.

Table S 10. Initial stiffness and Yield force evaluated after two consecutive 3 point bending test on: cylindrical double-layer composites after 2 months since irradiation, POP and FGC reference samples prepared by a registered technician

	First Bending test		**Second Bending test**		**Maintaining of the mechanical properties (second vs. first test)**	
	Initial Stiffness[a] (N/mm^2)	**Yield Force (N)**	**Initial Stiffness[b] (N/mm^2)**	**Yield Force (N)**	**Initial stiffness**	**Yield stress**
Double_LED_210S_#1	4.95	1.73	3.78	3	76%	173%
Double_LED_210S_#2	6.65	2.99	3.47	2.95	52%	99%
Double_LED_210S_#3	4.04	2.85	3.52	3.8	87%	133%
Double_LED_210S_#4	2.38	3.05	1.94	2.6	82%	85%
Double_LED_210S_#5	2.13	3.52	1.84	2.8	86%	80%
Double_LED_90S_#1	2.46	2.65	-	-	-	-
Double_LED_90S_#2	1.34	4.23	-	-	-	-
POP	333	23	-	-	-	-
FGC	72	40	-	-	-	-

[a] $R^2>0.99$
[b] $R^2>0.96$

Table S 11. Mass variation after harsh conditions exposure of double-layer composites.

	Hot humid environment	Cold humid environment	Soaked in water	Direct sun exposure
After exposure	1.03%	0.27%	21.72%	0.07%
1 hour after exposure	0.57%	0.03%	7.85%	-
17 hours after exposure	0.48%	0.12%	-0.90%	-
24 hours after exposure	0.44%	0.12%	-0.97%	0.55%