Supporting Information

Photopolymerization of zeolite/polymer based composites: towards 3D and 4D printing applications

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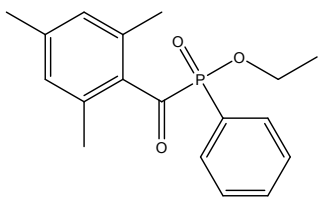
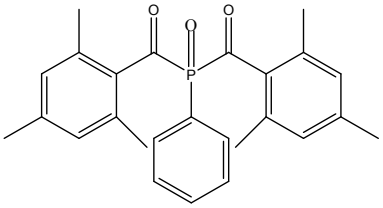
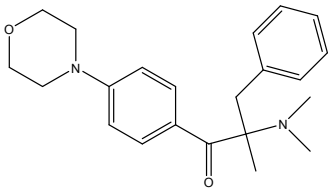
Scheme S1. Chemical structures of photoinitiators



TPO-L

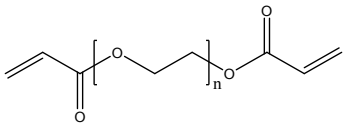


BAPO

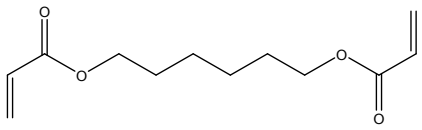


BDMK

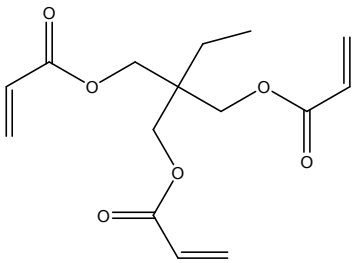
Scheme S2. Chemical structures of monomers



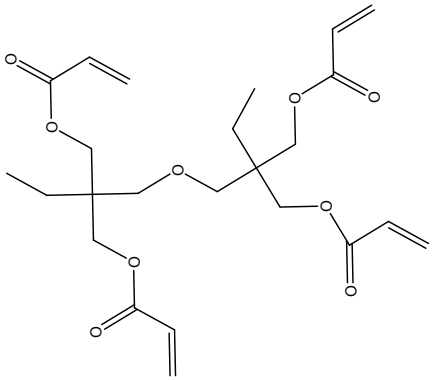
PEG-diacrylate



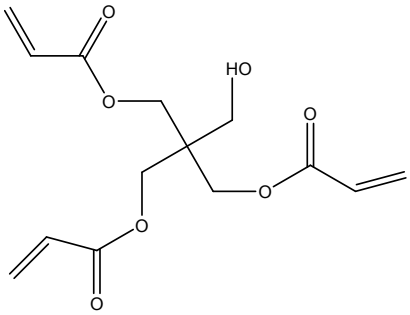
HDDA



TMPTA



TA



PETIA

Table S1. Details for the seven types of zeolites used as fillers in this work

Filler	Framework Type Code	Supplier	Si/Al	Na/Al	Crystal Size (av diam, μm)	Framework Density (T = Si, Al)
LTA-5A	LTA	Union Carbide	0.9	0.3	2.6	14.2 T/1000 Å^3
EMT	EMT	Self-synthesized	3.7	1.0	1.3	13.3 T/1000 Å^3
FAU1	FAU	Crossfield	2.7	1.0	0.6	14.2 T/1000 Å^3
FAU2	FAU	Zeocat	2.7	< 0.03	0.6	13.3 T/1000 Å^3
FAU-13X	FAU	Sigma-Aldrich	1.2	1.1	2.7	13.3 T/1000 Å^3
BEA1	* BEA	Clariant	88.0	-	0.3	15.3 T/1000 Å^3
BEA2	* BEA	Clariant	75.5	-	0.3	15.3 T/1000 Å^3

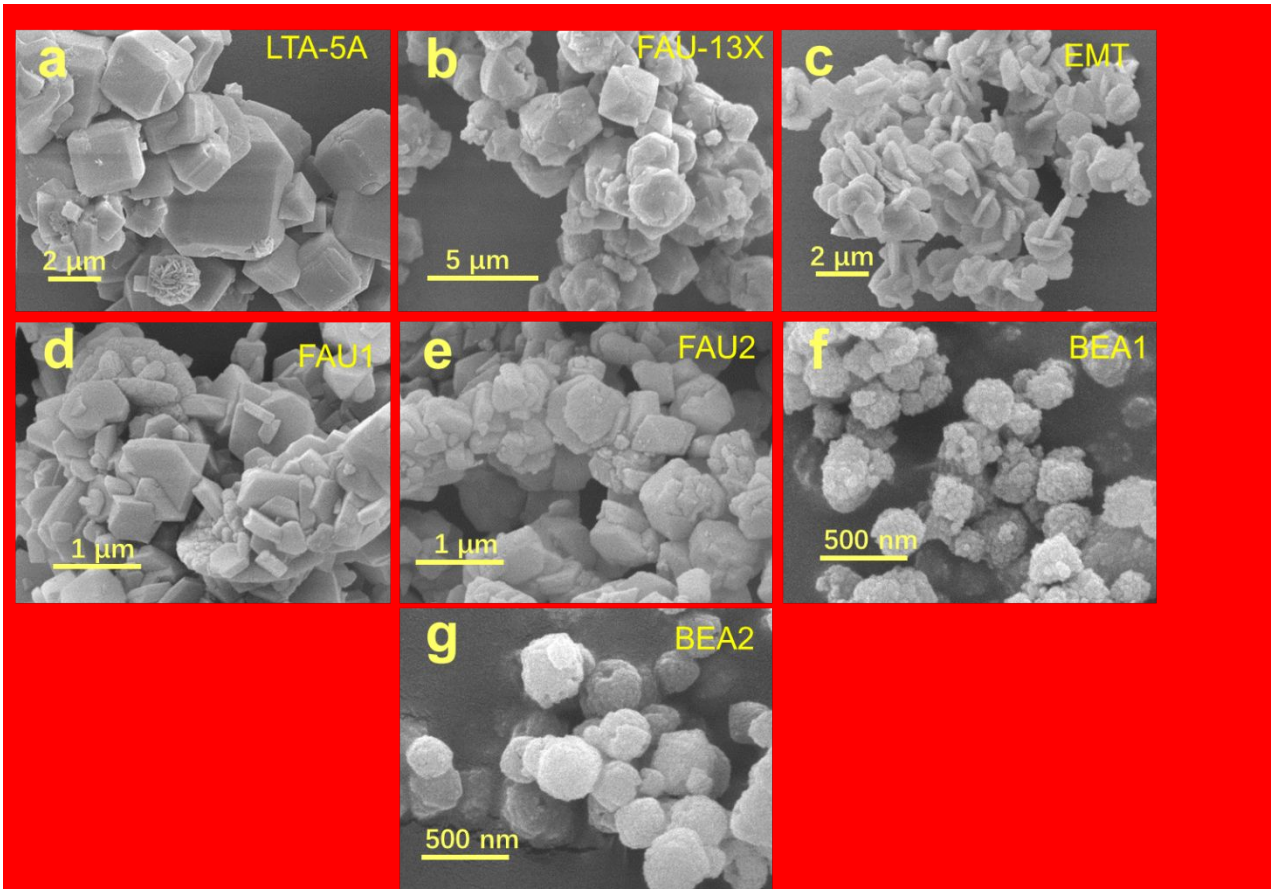


Figure S1. SEM images for (a) LTA-5A, (b) FAU-13X, (c) EMT, (d) FAU1, (e) FAU2, (f) BEA1 and (g)BEA2.

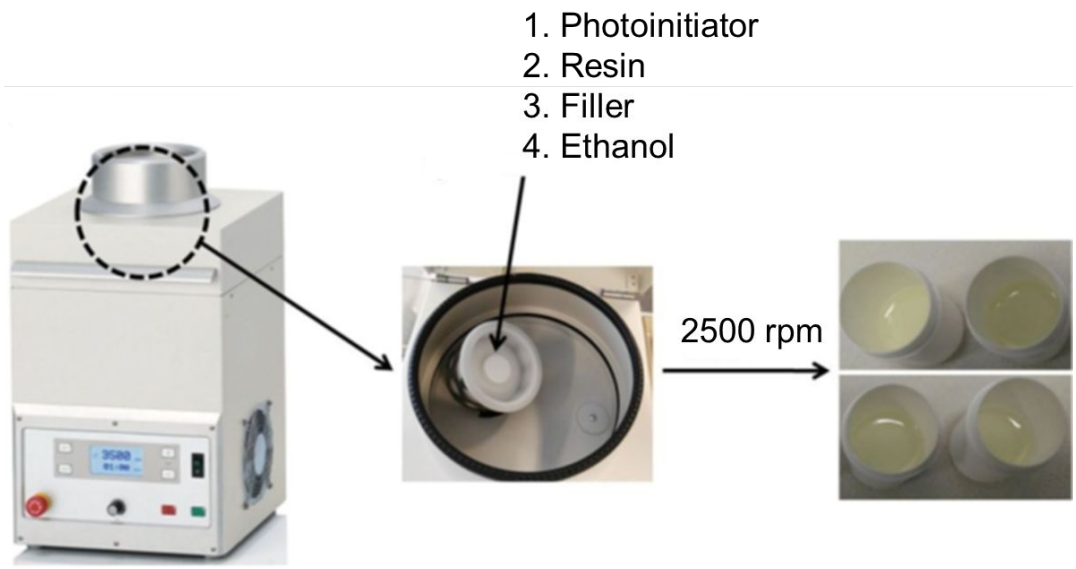


Figure S2. Experimental setup illustration for the homogeneous mixing of monomer, filler, photoinitiator and ethanol.

Table S2. Formulation used to prepare composites

Formulation	Monomer/ %	Filler/ %	Initiator/ %	Total sample/ g	Ethanol/ g [a]
1	90	9	1	2.22	/
2	79	20	1	2.53	/
3	66	33	1	3.03	/
4	49	50	1	4.04	/
5	39	60	1	5.05	/
6	32	67	1	6.12	/
7	29	70	1	6.73	/
9	24	75	1	8.08	0.513

[a]: After light-curing@405 nm, ethanol was removed by heating at 50 ℃ for 24 h for the access to high fillers content. Therefore, the weight of ethanol was not included in the total sample weight.

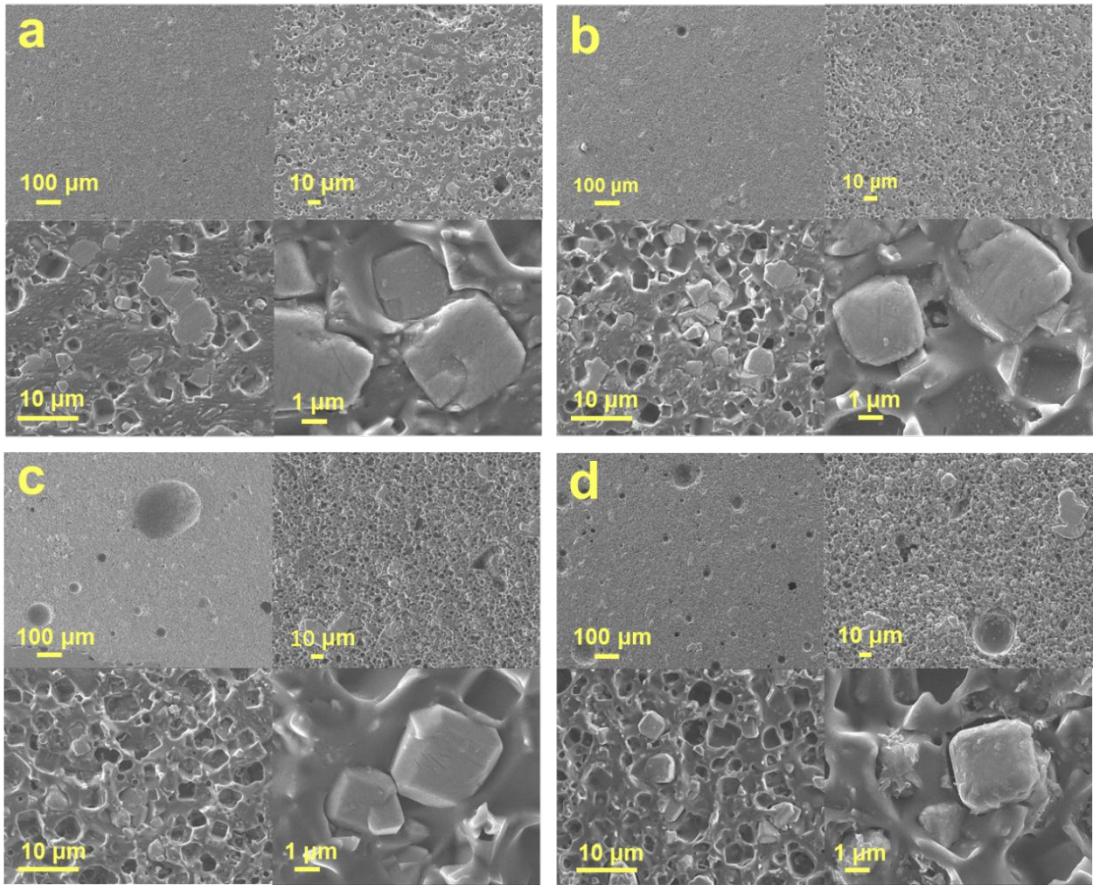


Figure S3. SEM images for composites containing LTA-5A: (a) PEG-diacrylate-LTA-5A @50%, (b) PEG-diacrylate-LTA-5A @60%, (c) PEG-diacrylate-LTA-5A @67%, (d) PEG-diacrylate-LTA-5A @75%.

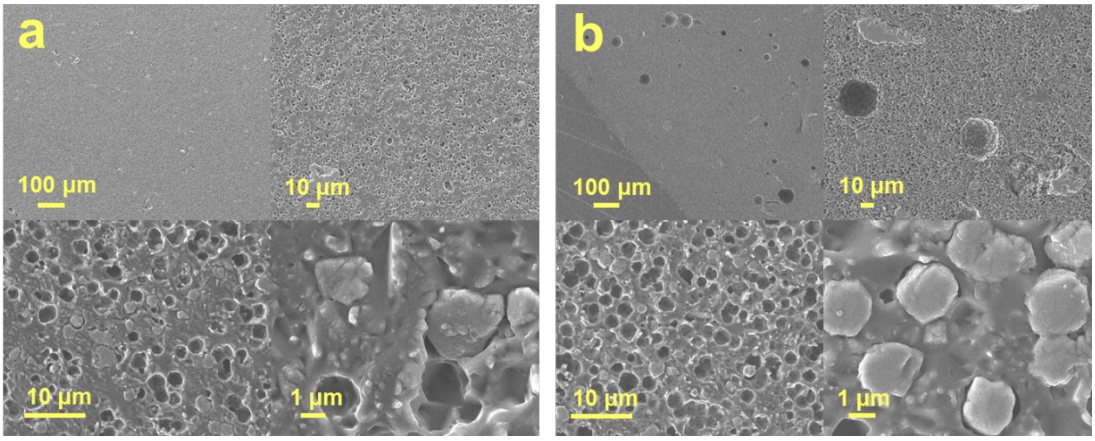


Figure S4. SEM images for composites containing FAU-13X: (a) PEG-diacrylate-FAU-13X@50%, (b) PEG-diacrylate-FAU-13X@60%.

Table S3. Weight loss values highlighted by TGA for LTA-5A, PEG-diacrylate and composite materials.

Filler (%) [a]	LTA-5A	0	9.0	20.0	33.1	49.3	59.4	66.0	69.3	74.2 [b]
T_{max} (°C) [c]	-	422	418	417	415	416	415	415	418	413
WL1 (%) (50-350°C)	16.0	0	1.7	4.0	5.2	7.2	8.2	9.5	9.0	12.0
WZC (%)	-	0	1.4	3.2	5.3	7.9	9.5	10.6	11.1	11.9 [b]
WL2 (%) (350-480°C)	0.4	95.3	88.0	73.1	61.9	47.7	39.3	33.2	30.2	25.2
MC (%)	-	98.9	90.0	79.0	65.9	49.6	39.6	33.0	29.7	24.8 [b]

[a] : calculated by taking into account the amount of zeolite, monomer and PI weighed to prepare the formulation (Table S1).

[b] : without taking into account of the ethanol that has evaporated after light-curing@405 nm.

[c] : temperature of the maximum decomposition rate.

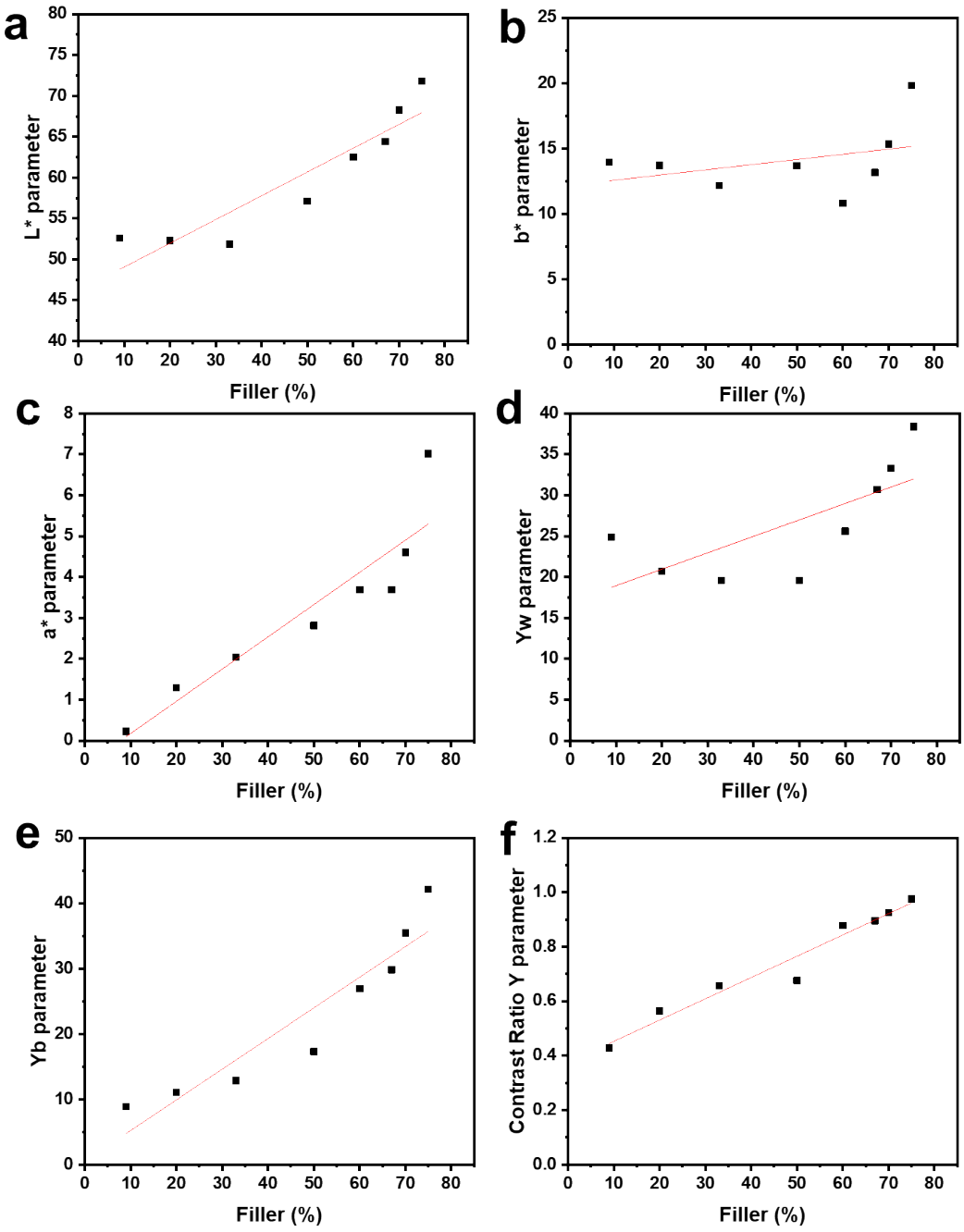


Figure S5. Colorimetric parameters vs. filler contents. (a) L* parameter vs. filler content; (b) b* parameter vs. filler content; (c) a* parameter vs. filler content; (d) Yw parameter vs. filler content; (e) Yb parameter vs. filler content; (f) Contrast Ratio Y parameter vs. filler content. Linear relationships are not expected.

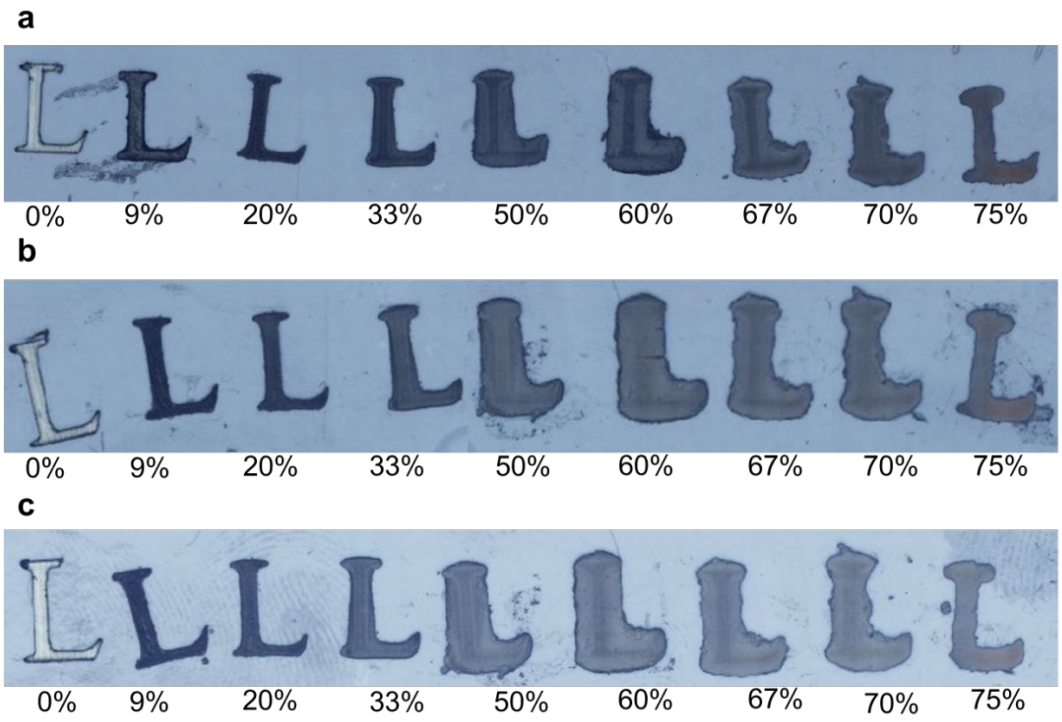


Figure S6. (a) NOM of composites containing LTA-5A before water swelling (b) NOM of composites containing LTA-5A after water swelling, (c) NOM of composites containing LTA-5A after heating at 75℃ for 4h (water removal).

Table S4. **The percentual variation of the volume for the comparison of the patterns in the cycle: starting (R_1), water swelling (R_2), water removal (R_3).** [1]

Filler (%)	0	9	20	33	50	60	67	70	75
R_1 (%)	0	0	0	0	0	0	0	0	0
R_2/ (%)	74.2	70.9	70.9	70.9	60.6	48.1	45.8	46.4	37.5
R_3 (%)	1.3	0	0	0	0	-3.3	2.3	3.7	0.9

[1]: The length, width and height of the letters were measured to calculate V_1 (starting volume), V_2 (volume after water swelling) and V_3 (volume after water removal).

[2]: The percentual variation of the volume (R) was calculated by equation: R_1=0 %, $R_2 = \frac{V_2 - V_1}{V_1} \times 100\ \%$, $R_3 = \frac{V_3 - V_1}{V_1} \times 100\ \%$.

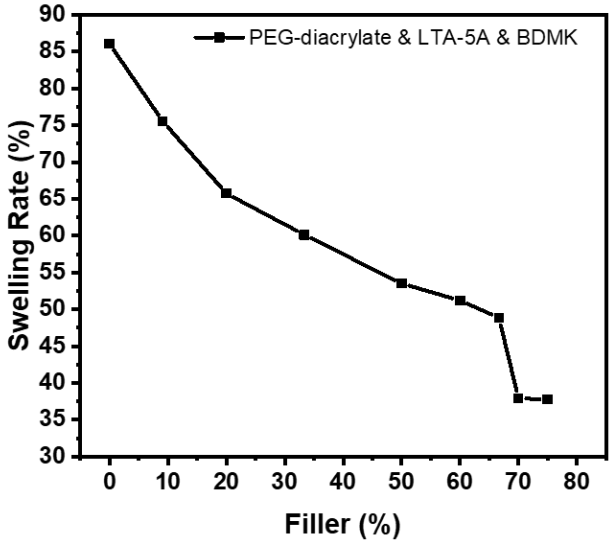


Figure S7. Water swelling property of composites containing LTA-5A (monomer: PEG-diacrylate; photoinitiator: BDMK; polymerization @405 nm).

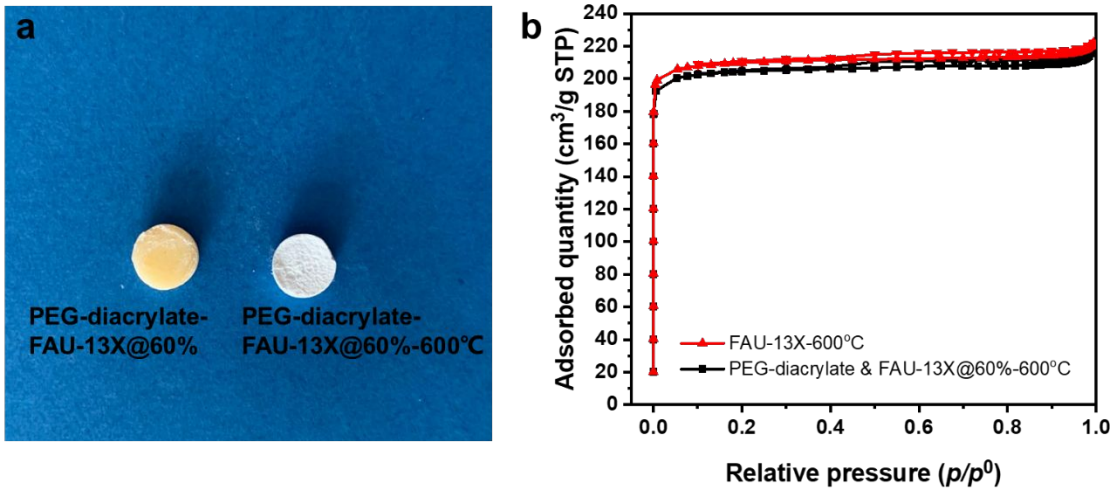


Figure S8. (a) Photos of PEG-diacrylate-FAU-13X@60% and PEG-diacrylate-FAU-13X@60%-600℃, (b) N_2 adsorption-desorption for FAU-13X and PEG-diacrylate-FAU-13X@60%-600 ℃.

Table S5. Surface areas for LTA-5A, PEG-diacrylate-LTA-5A@75%-600℃, FAU-13X and PEG-diacrylate-FAU-13X@60%-600℃.

	S_{BET}(m^2/g)	$S_{external}$ (m^2/g)	S_{micro}(m^2/g)	V_{micro} (cm^3/g)
LTA-5A-600℃	653	13	640	0.246
PEG-diacrylate-LTA-5A@75%-600℃	626	14	612	0.237
FAU-13X 600℃	859	6	853	0.324
PEG-diacrylate-FAU-13X@60%-600℃	834	14	820	0.311