Photopolymerization of zeolite filler-based composites for potential 3D printing application and gas adsorption applications

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Abstract

In recent years, photopolymerization has been found wide applications in industry and daily life, while many defective properties of polymers limit their development, including compressive strength, mechanical properties and functions. Furthermore, zeolites are microporous solids with many industrial applications. As fillers they can improve mechanical properties of zeolite/polymer composite and transfer their properties to composites. Here we reported the fabrication of composites with very high filler contents (80-95 wt%) under mild photopolymerization conditions (visible LED light irradiation, room temperature, under air). Compared to pure poly(ethylene glycol) diacrylate (PEGDA) polymer, mechanical properties have been greatly improved, and the storage modulus increased by nearly 20-fold compared to that of pure polymer. After debinding/sintering of composites by high temperature treatment, zeolite porosity is preserved with good adsorption capacities. Some step-like object with 3D structure was also obtained by an original 3D printing technique noted “layer by layer Molding/Curing”. Hence, as a great breakthrough, this work is expected to lead to a valuable development in the field of photopolymerization in quite highly filled composites. This also will expand their potential applications for 3D printing in the fields of high-performance lightweight materials and adsorption, and opens the door to a new process of zeolite shaping.

1. Introduction

3D printing, an additive manufacturing (AM) technique, recently has been developed in many fields, such as electronic industry,^[1, 2] adsorption and separation industry,^[3, 4] biomedicine industry,^[5-7] and etc. As the most common materials, polymers are used to applied in 3D printing field for their diversity and ease of adoption to different 3D printing processes.^[8-11] As an interesting approach for 3D printing, photopolymerization has many specificities, such as high production rate, low energy consumption, and excellent spatial and temporal control.^[12] Commonly, polymers formed by photopolymerization reactions, comprising a photoinitiating system (PIS), a polymerizable medium (M), and a light source (S).^[13-16] Therefore, photopolymerization is one of the most common polymerization methods applied in 3D printing industry.^[17-20] Pure polymer products obtained by 3D printers are only often used for conceptual prototypes, due to their inherent lack of appropriated mechanical properties and functionality.^[13, 21] To improve the mechanical properties and enhance functionalities of 3D printed objects, different types of filler are selected to polymers to form different kinds of composite materials, such as fibers^[22, 23], particles^[24-26] and nanomaterials^[27, 28]. There are also many researchers developing UV-curable particle-free ceramic compositions for stereolithography-based 3D printing technologies, which is a potential alternative to the common particle-based compositions.^[29] For example, SiOC ceramics with varied lattice structures can be produced using different polysiloxanes as preceramic polymers (PCPs) via photopolymerisation-based digital-light-processing 3D printing and pyrolysis.^[30] However, inorganic fillers such as zeolite are not able to obtain corresponding materials by such technology now, due to the filler's complex manufacturing process factors. In addition, there are several other elements to affect mechanical properties and functionalities of 3D printed polymer via photopolymerization, e.g. dye as photoinitiator,^[31, 32] oligomer/monomers^[33].

Zeolites are microporous crystalline aluminosilicates with a high specific surface area. These molecular sieves have a lot of applications as catalysts in petrochemical industry and environmental protection for example.^[34-36] In recent years, more and more researchers are working to combine zeolite as fillers with polymers to produce composites or hydrogel composites applied in medicine industry,^[37, 38] adsorption and separation industry.^[39, 40] Zhang et. al.^[3] used 5A zeolite raw powder as filler, bentonite as binder and photosensitive resin to obtain hierarchical zeolite monoliths by digital light processing (DLP)

technique, which can be applied in the field of CO₂ adsorption. Thakkar et. al.^[39] incorporated zeolite (0-30 wt%) into the polymer matrix, and added amine moieties into the polymer composite. These composites have robust structures with good mechanical integrity and comparable adsorption for CO₂ adsorption. Merilaita et. al.^[41] successfully obtained a hierarchically porous ZSM-5 zeolite structure with adsorption capabilities via stereolithography. In these slurries, the maximum content for zeolite could reach up to 55 vol%. After thermal treatment (debinding), the BET surface area analysis showed that the pore properties and surface area of the zeolite were not lost during manufacturing and debinding processes. However, the preparation of composites with high zeolite content through photopolymerization and the corresponding applications have been rarely reported, due to the light absorption and/or scattering by the fillers, which is a huge challenge of efficient photocuring.

In our previous work, we mainly studied the photopolymerization of zeolite/polymer composite (the photopolymerization kinetics and the depth of cure for composites),^[42] the mechanical and functional properties of composites (zeolite maximum content ~75 wt%).^[40] In this work, the proof-concept study describes fabrication of zeolite-polymer composite with very high filler content (80-95 wt%) through photopolymerization, and the corresponding 3D-printed objects can also be obtained. Moreover, after debinding/sintering at the appropriate temperature, the material retains the zeolite porosity.

In published works, the zeolite filler content for composite via photopolymerization was around 30 vol% to 55 vol% or around 20 wt%.^[3, 41] Hence, to our best knowledge, this is the first time to propose this related work with highly filled composite, which can be seen as a real breakthrough in the fields of photopolymerization, 3D printing for composites and zeolite shaping. The polymerization results were evaluated mainly through the depth of cure (DOC), X-ray diffraction measurements (XRD), scanning electron microscopy (SEM), dynamic thermomechanical analysis (DMA), thermogravimetric analysis (TGA). Furthermore, composites with high filler contents were treated at high temperature through a debinding/sintering procedure and their porosity has been evaluated by N₂ adsorption-desorption experiments. Finally, CO₂ and water adsorption capacities were determined on composites after debinding/sintering process. The results clearly indicated that this fabrication of zeolite-polymer composites and 3D printing technique can be applied to prepare adsorbents in order to expand the application of these materials.

2. Experimental Section

2.1 Materials

The resin Poly(ethylene glycol) diacrylate (PEGDA, $M_w \approx 600$) was purchased from Sartomer (SR610). The monomer 1,6-Hexanediol diacrylate (HDDA), the photoinitiator 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (BDMK), the solvent (ethanol, toluene, acetone and acetonitrile), FAU-13X powder (FAU) and FAU-13X beads (8 to 12 mesh) were purchased from Sigma-Aldrich. LTA-5A powder (LTA) and LTA-5A beads (4 to 8 mesh) was obtained from Union Carbide and ACROS respectively. The dispersant BYK-555 and BYK-S706 were obtained from BYK Additives & Instruments, and their abbreviations are BYK-1 and BYK-2 respectively. The chemical structures of monomers and photoinitiator are listed in Scheme S1. Characteristics of zeolites are listed in Table S1 and Figure S1.

2.2 Preparation of Photocuring Composites

First of all, the oligomer PEGDA and the filler zeolite were added into a vial successively. Then 1.0 wt% photoinitiator BDMK (based the weight of PEGDA and filler) and solvent were added, and stirred through the Speedmixer (DAC 150.1 FVZ-K) with rotation speed at 2000 to 2500 rpm until a homogeneously dispersed filled resins were obtained. All of these mixture resins were preserved in the dark room before photopolymerization reactions. The formulations of composites and the specific code of composites are presented in Table S2.

In a LED-curing box, a mold filled with the investigated resin was placed vertically under the light (LED@405 nm for 30 s; 1 W/cm²) (Scheme 1). Then, the sample in the mold was washed by acetone to remove the unpolymerized part, and then was put in oven to vaporize the solvent (80 °C for 24 h). The polymerized part on the top were used to measure the Depth of Cure (DOC) with an Absolute LCD Digimatic Indicator (Mitutoyo). Thus, pellets were obtained.

Scheme 1. The different stages of composite preparation.

2.3 Layer by Layer Molding/Curing Experiment

The 3D molding technique employed in this work was “layer by layer molding/curing”. Firstly, the homogeneous filled resin was loaded in a mold, and the excess resin was removed with a scarper and the resin surface was smooth. Next, a flat composite layer was obtained after irradiation through LED@405 nm. Then, on the cured composite’s surface, the second flat composite layer was obtained through the same operation. After repeated operation several times, a 3D object can be obtained. Then, for evaporation of the solvent, the printed 3D object was put in oven at 80 °C for 24 h. As shown in Figure 1, the 3D structure object “stairs” was obtained finally. Hence, based on the characteristics of the resin, these formulations in this work can have a potential application in the field of 3D printing via photopolymerization with high depth of cure.

Figure 1. 3D structure objects of different composites: (a) PEGDA-LTA@80%; (b) PEGDA-LTA@95%; (c) PEGDA-FAU@80%; (d) PEGDA-FAU@95%.

2.4 Material Characterization

The zeolite crystals size and morphology and their corresponding composites were investigated by scanning electron microscope (SEM) with a JEOL JSM-7900F microscope. Thermogravimetric analyses (TGA) were carried out using a thermal analyzer (METTLER-TOLEDO TGA/DSC 3+) by heating from 30 to 600 °C at heating rate of 10 °C.min⁻¹ under nitrogen atmosphere (N₂ flow rate: 100 mL.min⁻¹). For Dynamic Thermomechanical Analysis (DMA), composites were polished to obtain pellet with a thickness of 1 mm, and then experiments were performed on Viscoanalyser METTLER DMA861 at a frequency of 1.00 HZ in the tensile configuration. Zeolite crystalline structures were identified by X-ray diffraction (XRD) measurements using a PANalytical MPD X'Pert Pro diffractometer operating with Cu K α radiation (K α = 0.15418 nm) equipped with an PIXcel real-time multiple strip detector (active length = 3.347 ° (2 θ)). The powder patterns were collected at 295 K in the range 3 < 2 θ < 70, step = 0.013° (2 θ), time/step = 220 s.

The diffractograms were analyzed by using the X'Pert HighScore software package and compared with documented diffraction patterns in the International Centre for Diffraction Data (ICDD) database.

Nitrogen (N₂) adsorption-desorption isotherms were performed at -196°C with a Micromeritics ASAP 2420 Instrument on composites after thermal treatments at 600°C and 700°C. Before each measurement, the samples were outgassed to a residual pressure of less than 0.8 Pa at 90 °C for 1 h and 300 °C for 15 h. Specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method ($0.01 < p/p^0 < 0.03$). Microporous volume (V_{micro}) and microporous surface area (S_{micro}) were calculated using the *t*-plot method. The external surface (S_{ext}) was obtained by subtracting S_{micro} from the total surface. Mesopore size distributions were calculated by the BJH (Barrett-Joyner-Halenda) method on the desorption branch of the isotherm.

2.5 Thermal Treatments

PEGDA-LTA@80% and PEGDA-FAU@80% composites were heated at 600 °C for 30 min. After this debinding/sintering step, samples named as PEGDA-LTA@80%-600°C and PEGDA-FAU@80%-600°C were heated at higher temperature (700 °C for 30 min.). After such a second thermal treatment, they were called PEGDA-LTA@80%-600°C-700°C and PEGDA-FAU@80%-600°C-700°C. As shown in Figure 2, the organic compounds were removed and the 3D composite object became white (color of zeolite) after thermal treatment. Compared to their corresponding 3D composite objects, there was no fracture on the surface of 3D objects and the 3D object after thermal treatment kept the same shape and structure with a low shrinkage about 3 vol% - 8 vol%

Figure 2. 3D objects of different composites after debinding/sintering process: (a) PEGDA-LTA@80%; (b) PEGDA-FAU@80%.

2.6 CO₂ Adsorption Measurements

The CO₂ adsorption capacity of the composites after thermal treatments has been achieved at 0°C with

a Micromeritics ASAP 2420 Instrument under 10^{-5} Pa. Before each measurement, the samples were outgassed to a residual pressure of less than 0.8 Pa at 90 °C for 1 h and 300 °C for 15 h.

2.7 H₂O Adsorption Measurements

Water adsorption-desorption isotherms were performed at 25 °C using a Micromeritics ASAP 2020 Instrument. Prior to water adsorption experiments, water was flash frozen under liquid nitrogen and then evacuated under dynamic vacuum at least 5 times to remove any gases in the water reservoir. The samples (50-100 mg) were outgassed under vacuum at 90 °C for 1 h and 300 °C for 24 h to remove physisorbed water. The water adsorption capacity was determined from water adsorption isotherms.

3. Results and Discussion

3.1 Depth of Cure

For light-cured composites, the depth of cure (DOC) is a very important property with a definition in our work as the thickness of materials cured adequately under irradiation @405 nm. In our previous work, we successfully obtained the composite with zeolite content up to 75 wt%.^[40] It is a challenge to manufacture the composite with higher zeolite content, because the depth of cure (DOC) is normally determined by the optical properties of filler and monomer during the photopolymerization process.^[43, 44] Due to the presence of fillers with different geometries and refractive indices, the light transmittance of filled formulations can be affected by the light absorption, the increasing and/or change in light scattering, and the refractive index mismatch between the polymer and the filler.^[13, 45-47] Simultaneously, the light transmittance also decreases with the increasing thickness of sample. Therefore, the change of light transmittance is a very complex phenomenon, affected by several processes. Hence, this work will be meaningful, if highly filled composites can be obtained through photopolymerization with good depth of cure (DOC).

Figure 3 includes the DOC values obtained with different monomers, solvents and dispersants. As shown in Figure 3.a, zeolites were combined separately with two monomers/oligomers and the DOC value for LTA-5A at 80 wt% was larger than that for FAU-13X. LTA-5A has a better performer in PEGDA system for the high DOC value than that in HDDA system. Low-molecular weight PEGDA normally can be used as a monomer with high reactivity. At the same time, this polyethylene glycol (PEG) based monomer can

also be employed as the dispersant to prevent particle agglomeration, which could improve the light penetration in the corresponding formulations. In addition, zeolite is hydrophilic, PEG-based monomers have probably a better chemical compatibility than HDDA. Hence, the combination of PEGDA and zeolite could have higher DOC values. Hence, PEGDA was chosen as the oligomer for the photopolymerization.

Compared to DOC values from FAU-13X filled composite with different solvents, DOC values of LTA-5A filled composites were higher. It should be noted that different types of solvent affected the DOC values obviously (Figure 3.b), especially toluene. The DOC value of LTA-5A filled composite (80 wt%) was 2.3 mm, which was far superior to the results for other solvent. In order to further enhance the dispersion of zeolite in the mixture, BYK-1 and BYK-2 were added to FAU-13X filled composites with different solvents. As shown in Figure 3.c, when the BYK-1 or BYK-2 were combined with acetone or acetonitrile, 1 wt% of dispersant can improve the DOC value obviously. However, the corresponding DOC values could be concerned as falling within the error window, which meant the increase in DOC might not be directly related to the amount of dispersant (1%). Overall, the increase of dispersant (from 1% to 3%) did not have an obvious improvement on the DOC value in consideration of the error area. However, the DOC value was the largest with toluene when no dispersant was added. This can be explained by the influence of dispersant on the cross-link of PEGDA polymer during the photopolymerization process. In addition, the DOC value also could be affected by the light absorption during the process of photopolymerization. Hence, the combination of toluene and PEGDA without dispersant was the best in this work, which could give a better light transmittance for these composites with such high filler contents to have a better DOC through photopolymerization.

In order to determine the influence of zeolite content on the DOC value, the filler content has been increased. DOC values decreased continuously with an increase of the filler content. Finally, we successfully obtained the composite with 95 wt% zeolite (See Figure 3.d, DOC values for filler content up to ~ 60 wt% for FAU-13X and up to ~ 60 wt% for LTA-5A are referenced from our previous work.^[40]).

In one of our other previous works^[26], we successfully introduced iron powder into resin (TMPTA and PEGDA respectively) to obtain composites via photopolymerization. However, the DOC values of composites with 70 wt% (the maximum of filler content) were only 0.098 mm (TMPTA) and 0.105 mm (PEGDA) respectively. Hence, compared to the work about iron-based composites, this work has great advantages and improvements in the field of photopolymerization of thick composite samples.

To the best of our knowledge, this work reports the highest zeolite content in photopolymerized

composites (95% w/w corresponding to ~97 % in volume for PEGDA-LTA@95% and ~97.8 % in volume for PEGDA-FAU@95%).

Figure 3. DOC for different factors of polymerization: (a) 2 types of monomer (Ethanol was used as the solvent.); (b) 4 types of solvent; (c) 2 types of dispersant combined with different types of solvent in FAU based formulations (The filler content was kept at 80 wt%.); (d) DOC at different filler contents (DOC values for filler content up to ~ 60 wt% both for LTA-5A and FAU-13X come from reference ^[40]).

3.2 SEM and Particle Size Analysis

The zeolite crystals size and crystals dispersion in the composite were analyzed by SEM. LTA-5A crystals are characterized by well-shaped cubic morphology (Figure 4, Figure S2). The easily recognizable twinned octahedra reveal the common crystal shape of the cubic FAU-13X (Figure 5, Figure S3). Each crystals type has an average size (diameter) of 2.6-2.7 μm .

As shown in Figure 4, the LTA-5A zeolite is well dispersed at the surface of the composite even with a 95 wt% filler content. However, few small crystals aggregates (few μm diameter) and bubbles/voids appeared. The presence of aggregates is more evident with LTA-5A while bubbles are most observed for FAU-13X. Their presence could be related to the air trapped in filler aggregates before the mixing process

of filler and PEGDA. Also, this could be related to the viscosity of the mixture which made difficult to evacuate air during high-speed mixing.

SEM images with the most important magnification reveal a very good coating of the filler by the polymer.

Figure 4. SEM images of PEGDA-LTA@95%: (a), (b) and (c) surface of PEGDA-LTA@95%; (d), (e) and (f) cross-section of PEGDA-LTA@95%.

Figure 5. SEM images of PEGDA-FAU@95%: (a), (b) and (c) surface of PEGDA-FAU@95%; (d), (e) and (f) cross-section of PEGDA-FAU@95%.

3.3 Dynamic Thermomechanical Analysis (DMA)

The results of DMA are reported on Figure 6 and they complement those already published by our team. ^[40] Compared to the pure PEGDA polymer, the elastic modulus (G') and loss modulus (G'') for LTA-5A- and FAU-13X-containing composites at 25 °C increased. Well dispersed fillers with good interactions with polymer improve G' , because of the increase of constrains of the segmental motions of the

polymeric chain in the network. In addition, they can even improve the ductility because of their small size not creating large stress concentrations. When the filler content is 80 %, composites have the largest G' values for LTA and FAU. For PEGDA-LTA@80%, the G' and G'' reached up to 106.9 MPa and 6.7 MPa respectively. For PEGDA-FAU@80%, the G' and G'' reached up to 94.8 MPa and 5.3 MPa respectively. Compared to our previous work,^[26] the G' values of LTA-based composites are higher than that of iron-based composites when the same resin (PEGDA (SR610)) was employed, which means that zeolite matrix composites not only have better depth of cure (DOC), but also have advantages over iron powder matrix composites in mechanical properties.

Figure 6. DMA for (a) PEGDA-LTA and (b) PEGDA-FAU composites with different filler contents (DMA results for filler content up to ~60 wt% both for LTA-5A and FAU-13X come from reference [40]).

3.4 Thermal Stability of Composite

In order to determine the influence of the filler on the thermal stability of the composite, thermogravimetric analyses were carried out on composites with different filler contents.

As reported in Figure 7 and Tables S3 and S4, zeolite and PEGDA as received are characterized by two weight losses observed between 30 and 350 °C (water desorption), and between 350 and 600 °C (decomposition of PEGDA and water desorption from dehydroxylation reaction in zeolite). Here, WL1 and WL2 were defined as the weight loss associated to water desorption and PEGDA polymer, respectively. MC was defined as the amount of monomer used to prepare the composite.

In composite, these two weight losses are combined. The first weight loss increased logically up to 18.1 % and 20.1 % for composite with 95 % filler content with LTA-5A and FAU-13X respectively (WL1 in Tables S3 and S4). These values are close to the hydration rates of pure zeolites (17.2 % for LTA-5A;

22.3 % for FAU-13X). The value of the second weight loss is also in good agreement with the amount of monomer used to prepare the composite (WL2 and MC in Tables S3 and S4). The zeolite contents in the residue recovered at 600 °C were estimated to 99.0 %, 99.6 % and 99.8 % for LTA-5A composites and 98.9 %, 99.5 % and 99.7 % for FAU-13X composites with an initial zeolite content of 80 %, 90 % and 95 % respectively. The other part corresponds to carbon deposits resulting from the decomposition of the polymer.

The temperature ($T_{\max}$) of the maximum decomposition rate (Figure 7.b and Table S3 for LTA-5A, Figure 7.d and Table S4 for FAU-13X, the inflection point for each curve) does not significantly change with the addition of zeolite. Hence, the filler addition does not have a significant effect on the thermal stability of the composite.

Figure 7. TGA and DTG (derivative of TGA) curves for (a) and (b) LTA-5A powder, pure polymer and LTA-5A filled composites; (c) and (d) FAU-13X powder, pure polymer and FAU-13X filled composites.

3.5 Zeolite Structure Stability

The stability of the zeolite structure in composites was controlled by XRD. As reported in Figure 8 for 80 wt% filler content, the XRD patterns of composites were similar respectively to those of the zeolite powder in agreement with the literature^[48, 49]. After thermal treatments, lattice parameters vary by less than 0.2% proving the zeolite structure stability (Table S5).

Figure 8. XRD patterns of (a) LTA-5A powder, PEGDA-LTA@80%, PEGDA-LTA@80%-600 °C, PEGDA-LTA@80%-600 °C-700°C and reference pattern for LTA structure (ICDD 04-017-3644); and (b) FAU-13X powder, PEGDA-FAU@80% PEGDA-FAU@80%-600°C, PEGDA-FAU@80%-600°C-700°C and reference pattern for FAU structure (ICDD 00-038-0237).

3.6 N₂ Adsorption-Desorption Isotherms

Nitrogen sorption measurements at - 196 °C were undertaken to evaluate the textural properties of zeolites and composites after thermal treatments (after debinding/sintering).

The isotherms of zeolite powders reported on Figure 9.a and 9.b are type I characteristic of microporous compounds according to the IUPAC classification of isotherms.^[50] The large adsorption capacity observed at $p/p^0 = 0.1$ shows the capacity to adsorb nitrogen even as traces. A hysteresis loop (H4 type) only visible for LTA at relative pressure of 0.4-0.8 (isotherm type IV) reveals the presence of mesopores with pores diameter of 3.8 nm (Table 1) due to the industrial synthesis process or to crystal agglomerates.

Textural properties were also evaluated after thermal treatments at 600 °C and 600°C-700°C for composite with 80 % filler content which exhibits the best mechanical properties. They refer to grams of

zeolite.

As reported in Table 1 and compared to powder, microporous surface and volume decreased with an increase of the temperature for FAU-13X zeolite: the values were reduced by ca. 28 % and ca. 57 % at 600 °C and 700 °C respectively. At the same time, mesopores were formed and their diameter increased with the temperature (from 3.8 nm-5.6 nm to 11.9 nm, Table 1). In these materials with hierarchical structure, mesopores shape changed from ink bottle geometry (H2b hysteresis loop at 600 °C) to coexistence of opened pores with partially blocked pores (H5 hysteresis loop at 700 °C). As observed on TEM images (Figure S4), mesopores are formed during the polymer decomposition and appear to be localized in the carbonaceous residue observed on the zeolite crystals surface. The textural properties of calcined composites are inferior to those of commercial beads used as reference but only slightly lower for composite calcined at 600 °C.

The behavior of LTA 5A zeolite is different. The temperature of the thermal treatment didn't significantly alter the textural properties of the composite (Table 1) which are only ca. 5 % lower than those of the powder. This could be explained by the low residual carbon which would partially block access to micropores. Thus, composites have average V_{micro} and S_{micro} of $0.23 \text{ cm}^3 \cdot \text{g}^{-1}$ and $603 \text{ m}^2 \cdot \text{g}^{-1}$ respectively. Mesopores diameter remains at 3.8 nm. Such porous materials have microporous characteristics ca. 38 times higher than those for commercial beads used as reference. These last one have higher mesopores diameter (20.9 nm; 48.1 nm) and S_{ext} ($78 \text{ m}^2 \cdot \text{g}^{-1}$) because of inter-particle void spaces.

It therefore appears that calcined composites have interesting porous volumes that would allow them to be used as adsorbents.

Figure 9. N₂ isotherms for (a) LTA-5A powder, PEGDA-LTA@80%-600°C, PEGDA-LTA@80%-600°C-700°C and LTA-5A beads; and (b) FAU-13X powder,

PEGDA-FAU@80%-600°C, PEGDA-FAU@80%-600°C-700°C and FAU-13X beads.

Table 1. Textural properties of zeolites (powder) and composites (@80%-600°C and @80%-600°C-700°C) determined after N₂ adsorption-desorption.

	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	S_{external} ($\text{m}^2 \cdot \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \cdot \text{g}^{-1}$)	Mesopore diameter (nm)
LTA-5A	651	21	630	0.24	3.8
PEGDA-LTA@80%-600°C	610	15	595	0.23	3.8
PEGDA-LTA@80%-600°C-700°C	620	9	611	0.23	3.8
Commercial LTA-5A Beads	546	78	436	0.17	20.9 ; 48.1
FAU-13X	853	4	849	0.32	-
PEGDA-FAU@80%-600°C	641	39	602	0.23	3.8 ; 5.6
PEGDA-FAU@80%-600°C-700°C	388	24	364	0.14	11.9
Commercial FAU-13X Beads	681	49	632	0.24	29.0

3.7 CO₂ Adsorption Analysis

The CO₂ adsorption isotherms are depicted in Figure 10 and adsorption capacities ($\text{mmol} \cdot \text{g}^{-1}$) are reported in Table S6. For each zeolite, rapid low-relative pressure adsorption can be observed revealing a rapid adsorption in micropores.

The measured CO₂ uptakes ($p/p^0 = 0.030$) of LTA-5A powder, PEGDA-LTA@80%-600°C and PEGDA-LTA@80%-600°C-700°C are 113, 106, 107 $\text{cm}^3 \cdot \text{g}^{-1}$ respectively (Figure 10.a) showing that the temperature of the thermal treatment has no significant influence on the adsorption capacity. The values for the calcined composites are only 6.2 % lower than that of powder but 23 % higher than that of commercial

beads. This can be explained by the low residual carbon which would partially block access to micropores. Simultaneously, the LTA-5A commercial beads had less micropores and low BET surface areas than both LTA-5A powder and our corresponding materials. For FAU-13X zeolite, the CO₂ adsorption capacity decreased when the temperature of the thermal treatment increased (- 24 % at 600 °C and - 45.3 % at 700 °C compared to powder). This can be also explained by the presence of residual carbon that would partially block access to micropores but also by lower thermal stability of the FAU structure. However, the adsorption capacity of PEGDA-FAU@80%-600°C is comparable to that of the commercial beads (ca. 116 cm³·g⁻¹).

Hence, calcined composites are potentially interesting for CO₂ adsorption.

Figure 10. CO₂ isotherms for (a) LTA-5A, PEGDA-LTA@80%-600°C, PEGDA-LTA@80%-600°C-700°C and LTA-5A beads; and (b) FAU-13X, PEGDA-FAU@80%-600°C, PEGDA-FAU@80%-600°C-700°C and FAU-13X beads.

3.8 H₂O Adsorption-desorption Analysis

As zeolites are well-known as desiccants in humid atmospheres, water adsorption capacity of calcined composites has been determined. It was determined from water isotherms reported in Figure 11. Types I and IV isotherms characteristic of adsorption in micropores and mesopores respectively are observed as for the N₂ adsorption. Until relative humidity (RH) of 92 % ($p/p^0 = 0.92$ on the isotherms, Figure 11), adsorption capacity of calcined composites is higher than that of commercial beads whatever the zeolite (+ 17.4 % for RH = 50 %, + 21.7 % for RH = 30 %). For example, the adsorption capacity of PEGDA-LTA@80%-600°C and PEGDA-FAU@80%-600°C at RH = 50 % is 26.1 wt% and 30.3 wt% respectively, and 18.4 wt% and 22.1 wt% for corresponding commercial beads, respectively (Table S7). Saturation water adsorption capacity (for relative humidity (RH) of ca. 100 %, $p/p^0 = \text{ca. } 1$) is higher for

commercial beads because of adsorption in interparticules mesoporosity. While the adsorption capacity of PEGDA-LTA@80%-600°C-700°C and PEGDA-FAU@80%-600°C-700°C at RH = 50 % is 21.6 wt% and 23.2 wt% respectively, which means that the thermal treatment with higher temperature (700 °C) resulted in the lower water adsorption property, micropores being partially blocked by the low residual carbon and the FAU zeolite structure being probably slightly less stable thermally.

Hence, composites after calcination at 600 °C or 700 °C possess high enough water adsorption rates to consider them as dessicants.

Figure 11. H₂O adsorption and desorption isotherms for PEGDA-zeolite@80% after thermal treatment at 600 °C, 600°C-700°C and corresponding commercial beads for (a) LTA-5A and (b) FAU-13X type zeolites. Only adsorption isotherm is reported for commercial LTA 5A beads.

4. Conclusions

In this work, we have successfully obtained photo-composites containing very high zeolite filler contents (80-95 wt%) at 405 nm LED irradiation under mild conditions. After photopolymerization, there was no negative influences on the crystal structure of zeolites. Composites with LTA-5A had better DOC values (better light penetration) and mechanical properties which means that LTA-5A/PEGDA was the best combination. Moreover, the microporous characteristics of these last composites after thermal treatments and of PEGDA-FAU@80%-600°C do not vary significantly compared to the parent zeolite powders. Thus, they retain all the adsorption potential of zeolites as for water and CO₂ for example.

This work would not only promote the development of the effect of zeolites on photopolymerization, but also find important potential applications of photopolymerization reactions in the fields of

high-performance light-weight materials, medicinal materials, 3D-printing, adsorption materials, and so forth. It also opens the way to a new method of adsorbent shaping.

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Notes

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Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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