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Facile Fabrication of Porous Open-Cell Polymer Structures from Sacrificial "Natural Templates" and Composite Resins

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Abstract

In this paper, we investigate several types of "natural or bio sourced templates" (sugar, salt, bone, coral, PLA 3D-printed scaffolds) for a simple elaboration of macro porous thermoplastic or thermosetting polymers, especially based on resins commonly used in composites manufacturing. Open-cell, macro porous polymer foams are obtained from resin impregnation of a template. Process consists of 3 simple steps: a) impregnation/infiltration/infusion of the template, b) polymerization of the resin, c) removal of template, mainly by water.

We compared several resins and showed that a low viscosity and a sufficient wettability enable fast impregnation of templates, where impregnation times are <4 min for samples on 10 to 30 mm thicknesses. The resulting polymeric porous structure is the overall replication of the template, exhibiting mainly open pores in the range of 100 to 500 µm, and densities from 0.25 to 0.4 g/cm3. Such open foams behave as sponges and can (re) absorb liquids either polar (water) or alcohols or silicon oil, which are filling the entire void volume. The resin filling step is valuable to introduce additives or functions in the foams (here an impact modifier is tested).

Keywords: Bio templates; Composites resins; Replication; Sugar templating; Foams; Infusion; Macro cellular polymers

Introduction

Porous scaffolds and open cell porous matrices are known for many materials. Some of them have been used as sacrificial templates to produce other porous (inorganic or organic) materials from a well-defined matrix (the template) [1-3]. In this type of process -"replication", "hard templating", the first step is impregnation or infiltration of a porous matrix by a component and its consequent solidification, followed by the removal of the template matrix through extraction, dissolution, or selective degradation. The "replication" method is a rather simple fabrication process and ensures the direct control of morphological parameters, such as the density, void content, void size, rigidity of the resulting foams, and dimensions of foamed pieces.

In the field of polymers, light-weight materials [1-3] with nano to macro porous open cellular structures can collapse/deform (mechanically), or absorb/separate liquids. Applications are classically damping materials, energy absorbing structures, thermal insulators, sponges, catalysis media, filtration media and membranes. Many papers have been published on porous replicated polymers from sacrificial templates [1-3]; the reported studies are often concerned by small pore sizes and the processes are sophisticated.

Sacrificial templating is first well known in the fabrication of metal foams [4-9] and of ceramic foams or carbon foams [3,10-12].

As far as bio based or natural templates are concerned, studies used water leachable templates: salt (NaCl) particles [4-9,13] or sugar grains [14-23], and more rarely other types of templates (e.g coral, PLA) [10,12,24]. For organic polymer replicates, authors proposed several processing methods, for different applications, with various polymers.

Different applications are targeted [10-12,15-23,25,26]: i) scaffolds in the medical field, such as bio active scaffolds for cell growth, bone reconstruction, tissue engineering; ii) media for selective liquid absorption such as oil removal from water [25], membranes, or organic pollutant capture, iii) optical and energy applications.

(iv) An original and recent example [14] is the infusion of a sugar cube with a silicone polymer solution to create a 3-D porous silicone substrate, helping to reduce lithium dendrite growth in batteries, otherwise a source of early aging. Metallic nano particles-filled PDMS, infused in a sugar template, provide a regular particles' network trapped in PDMS after removal of the template for plasmonic optical applications [23].

(v) Nafion ions were directly introduced in a PDMS resin for exchange composite membranes by Festarini et al. [22] to improve compatibility between components of devices for energy transport. Kellenberger at al. [26] used Ca or Sn carbonate soluble nanoparticles (≈50 nm) dispersed in PES to fabricate porous ultrafiltration membranes. Shahidi et al. produced membranes by a continuous extrusion process and salt leaching [13].

(vi) Capes et al. [17] fabricated single or multi layered regular scaffolds from packing of sugar calibrated spheres infiltrated by polyglycolide for tissue engineering (60% vol porosity). Patrick et al. [24] proposed PLA fibers mixed with tin oxalate micro particles for PLA catalytic thermal degradation. PLA is first transformed into fibers then introduced in fiber-reinforced composites together with non-degradable fibers (glass, carbon) and/or a 3D PLA printed scaffolds. After PLA thermal degradation, the hybrid composites are 3D interconnected models of vascularization.

Polymer of medical interest (PLA, PCL, a poly(ether-ester)) were

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prepared in dioxane solutions and were filled into salt or sugar fused particles by Hou et al. [15], followed by freeze drying of the solvent, and subsequent water-leaching of sugar. Such a combined method (freeze drying+leaching) allows a high connectivity and porous volume (≥ 90%).

In oil removal products or oil spill devices, oil compatible porous poly dimethyl siloxane (PDMS) sponges have been often made from sacrificial templates (sugar, salt) [18,19,27]. However sugar templates may show a difficulty to be totally removed by water from hydrophobic PDMS; an alternative is ethanol-leaching of citric acid templates [19].

In this paper, we investigate several combinations of "natural or bio sourced templates" (e.g sugar, salt, bone, coral) and common composites resins for a simple elaboration of robust macro cellular thermoplastic or thermosetting polymers.

One intention is to compare and test polymerizable resins (commonly used in composites manufacturing) towards their ability to infuse (to impregnate) a template and to fully polymerize; and compare several leachable natural templates towards their ability to be impregnated and removed without changing the porous polymer matrix.

The method is low cost, easy to handle, robust, and applicable to many polymer precursors (monomers, oligomers, resins). Furthermore, the foams offer a functionalization capability, by either introducing functional agents in the liquid resin before infusion or by chemical modification of the foams*.

(**those materials are not strictly speaking "foams" because no foaming step occurs, there is no bubble growth, but the term "foam" is currently used for metal foams obtained from a replication technique*)

The objective is to validate a single technique with different polymeric resins (thermosets and thermoplastics) from different largely available templates; giving a range of rigid to flexible medium-density polymer foams. The general steps are shown in Figure 1. First food sugar, as commercial lumps or powder, was used as templates; then, sodium chloride (compacted NaCl), bone, coral, and finally 3D-printed PLA scaffolds were also used.

Experimental Part: Strategy of Choice

Natural templates and preforms

Templates are in the form of solid porous preforms. For each type of preform, mass and dimensions are measured accurately on 3 to 5 specimens. Since the shapes of the pieces are well defined, the density values are calculated from the measurements of mass and volume. The (apparent) density or volumetric mass (specific gravity) ρ (in g/cm^3) is measured by eqn. (1). Density of polymerized polymers is taken as 1.15 g/cm^3.

$$\rho = m/V \quad (1)$$

where m is the mass of a preform/template or a foam, V is the volume measured from dimensions.

Porosity or % of volumetric void X_{void} (%) is calculated by eqn. (2):

$$\text{Porosity}^{\text{preform/template}} = X_{void}^{\text{preform/template}} = [1 - (\rho \text{ preform/template}/\rho \text{ neat material}^{\text{template}})] \times 100 \quad (2)$$

The same relation is used to characterize the void content (%), or porosity, of the polymer foams in eqn. (3):

$$\text{Porosity}^{\text{polymer foam}} = X_{void}^{\text{polymer foam}} = [1 - (\rho\text{foam}/\rho \text{ neat polymer})] \times 100 \quad (3)$$

Sugar preforms

Commercial food sugar (cubes, lumps) is used as bought from supermarkets. It can come in the form of powder or either cubic, rectangular, or cylindrical shape, and from cane sugar ('brown' sugar) or beet sugar ('white' sugar). For each type of sugar lumps, mass and dimensions are measured on 5 different bits. "Sucrose" (saccharose, i.e D-glucopyranosyl-D-fructofuranose) is the main component of food sugar; $\rho_{sucrose}$ is taken as the theoretical value of 1.587 g/cm^3.

Additionally, other preforms were made from commercial sugar powder compacted in a home-made rectangular mold in order to obtain bars (thickness up to 10 mm, length up to 100 mm). Compaction is carried out with any kind of pressing tool on top of the mold with a compaction pressure of 10^4 Pa to 10^5 Pa (5 to 10 kg/10 cm^2). The piece is made by adding sugar powder layer by layer, spraying water between each layer, and drying the whole piece at 60°C for 5 hrs.

In the same manner, preforms up to 400x400 mm^2 were obtained.

Salt preforms

Sodium chloride preforms [4-6] were kindly provided by EPFL (A. Mortensen) in the form of cylinders. The salt preform presented in the paper comes from cylinders (30 to 40 mm diameter, height 200 mm) made by cold isostatic pressing, from 400 µm or 60-90 µm NaCl particles [4,8,9]. Replication using this salt for the production of metal foams is described in a practical way in ref [7]. The theoretical density of NaCl is taken as ρNaCl=2.16 g/cm^3.

Other natural templates as preforms

i) A bone, cut in a cow leg, in a nearly cylindrical shape, was given by a butcher; it was skinned, washed, bleached, rinsed with water, left in ethanol and dried before use.

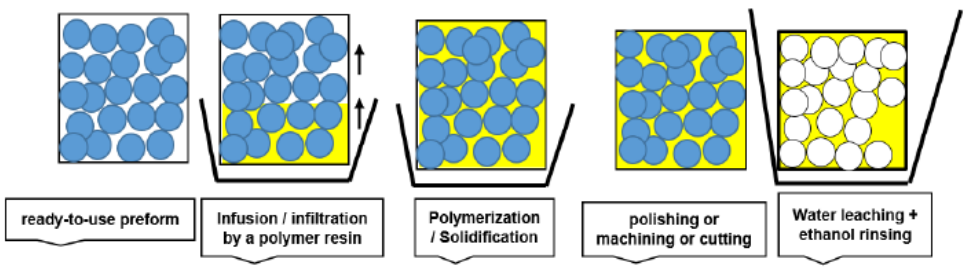


Figure 1: General processing steps used for the polymer replication of bio templates (the yellow color indicates resin filling, the blue circles stand for the template's grains, empty circles scheme the voids coming for template's grains).

ii) A coral (from the Red Sea) was used as received.

iii) PLA (polylactic acid, a biodegradable polymer) scaffolds were made by 3D printing in a special FDM printer (Fused Deposition Modeling) made to deposit narrow filaments (TechnoShop, IUT, université de Bordeaux, Dr M. Faessel). Figure 2a gives the models (Figure 2a(I)) and the 3D printed scaffolds (Figure 2a(II)), of overall dimensions 10x10x5 mm^3, named cubes 1 and 2. PLA reference is "eSun, blanc, 1.75 mm 1000 g". Filaments are 90°-crossline printed. The thickness of deposited filaments is set at 100 µm while the spacing between filaments is set respectively at 100 µm for cube 1 and 200 µm for cube 2, according to the models shown in Figure 2a(I). $\rho_{neat\ dense\ PLA}$ is taken as the theoretical value of 1.24 g/cm^3.

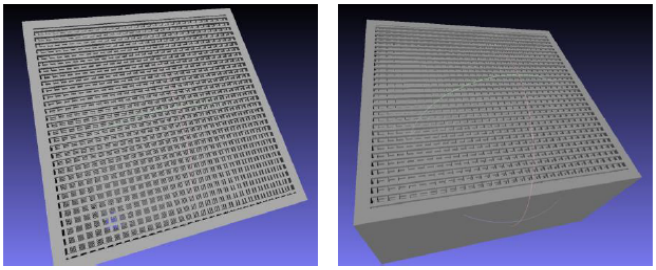


Figure 2a(I): Model to obtain 3D-printed scaffolds (example of cube 2).

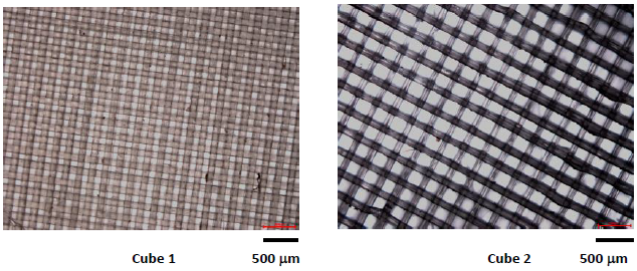


Figure 2a(II): 3D-printed PLA-scaffolds, cubes 1 and 2 cube 1 and 2 <=> template, before impregnation, observed by transmission optical microscopy.

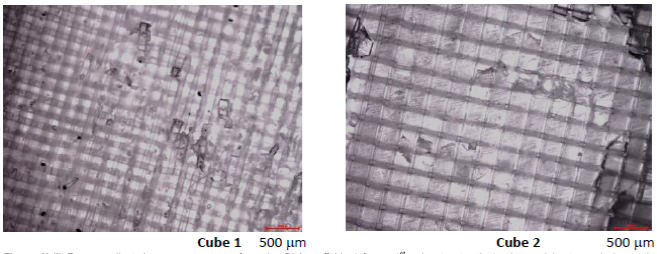
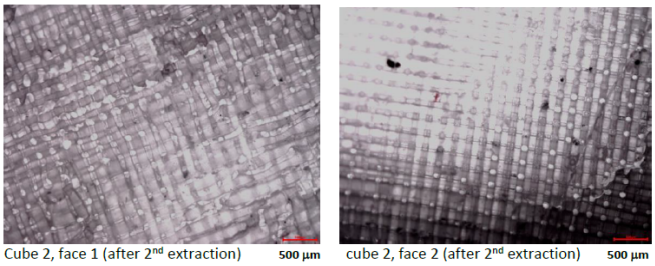


Figure 2b(I): Epoxy replicated porous structures from the PLA-scaffolds (after a 1st solvent extraction), observed by transmission optical microscopy (cubes 1 and 2).



Epoxy replicated porous structures from a PLA-scaffold after 2nd extraction, observed by transmission optical microscopy (cube 2).

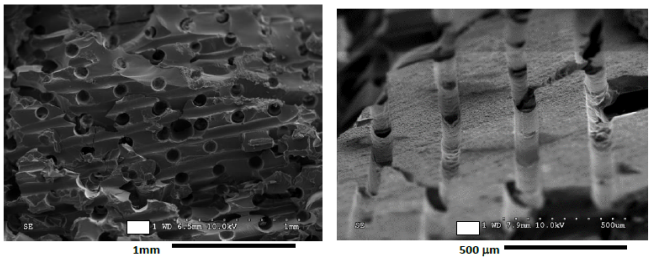


Figure 2b(II): Epoxy replicated porous structures from a PLA-scaffold, observed by scanning electron microscopy, Cube 2, core (after 2nd extraction).

Figure 2: Porous polymer replications from 3D printed scaffolds.

Morphologies

Morphologies were observed by digital microscopy (Keyence VHX-5000) or Scanning electron microscopy. We do acknowledge Keyence, Mr Charles du Mas de Paysac and Mr Julien Gutierrez for kindly carrying out the digital microscope observations on as received samples. Scanning electron microscopy (HITACHI model S-3000N), 10kV, WD=9 mm, is carried out on liquid nitrogen fractured samples that were coated with gold. Table 1 gives the templates characteristics: typical sample dimensions, apparent measured densities, and calculated void contents (%).

(a) If $\rho_{\text{neat dense NaCl}}$ is taken as a value of 1.9, see this value in ref [28], instead of the theoretical crystal value of 2.16, since the salt in the preform is not probably purely dense crystallized NaCl due to cold sintering, then the calculated void fractions of the used NaCl preforms (26%, 29%) are close to that mentioned in references [4,5,8] i.e 25% for a NaCl preform, precursor of metallic foams.

Choice of resins as impregnation systems, infiltration or infusion processes

The resins used in this study can be any of those used in the composites industry, especially in laminating, infusion or RTM processes [29,30]. Several epoxy resins (thermosetting) and one acrylic resin (thermoplastic) was chosen (Table 2). Liquid resin systems were

Template/Preform	Composition	Origin	Shape (initial ≈ final)	Typical Dimensions (mm)	**Density** (measured) (g/cm³)/ Porosity (calculated) (%)
Sodium chloride sintered	NaCl 400 µm	EPFL [4,5,8]	Cylindrical	~ Φ=20/=15	1.4 (35% => 26% [(a)])
	60-90 µm				1.35 (38% => 29% [(a)])
Cow bone	Mainly Calcium Phosphates (hydroxy apatite)	Butcher	trimmed as cubes	~15x15	Sample 1: ~0.70
					Sample 2: ~0.85
Coral	Calcium carbonates, Calcite, Aragonite, Conchyoline	The Red Sea	-	-	≈ 1.10
3D-printed scaffolds	PLA (polylactic acid)	FabLab IUT Bordeaux	Cubes 10x10x5 mm	Exp. Part and Figure 2a	Cube 1: 0.73 /41%
					Cube 2: 0.58/53%
Sugar lumps (commercial)	Sucrose	Super markets			
Cane sugar (brown sugar)			Cylindrical	*F*=17.3/=12.3	1.05 ± 0.025
					34% ± 2
Beet sugar (white sugar)			Rectangular	27.5x18x12	1.05 ± 0.02
					34% ± 2
Beet sugar (white sugar)			Cylindrical	*F*=17.3/=12.3	1.01 ± 0.015
					36% ± 1
Stevia sugar (white sugar)			Cubic	16x16x9.7	1.01 ± 0.025
					36% ± 2
Powder sugar (white sugar)		Compressed in a mold	Bars	Length: 30 to 100,	Variable
				Thickness: 4 to 10	

[(a)]If $\rho_{\text{neat dense NaCl}}$ is taken as a value of 1.9, see this value in [28], instead of the theoretical crystal value of 2.16, since the salt in the preform is not probably purely dense crystallized NaCl due to cold sintering, then the calculated void fractions of the used NaCl preforms (26%, 29%) are close to that mentioned in references [4, 5, 8] i.e. 25% for a NaCl preform, precursor of metallic foams.

Table 1: Templates characteristics: composition, typical dimensions, (apparent) measured densities, and calculated porosity (%).

Resin System	Name	**Molar Mass** (g/mol)			**Viscosity** (initial) (Pa.s)	T_g (final) (°C)
One-component thermoplastic resin	Elium®, methyl methacrylate-based resin, initiated with 1 wt% or 2 wt% BPO [(b)]	100			0.2	115
Bi-component thermosetting resin	Liquid Mixture	Molar Mass of Hardener (g/mol)	Molar Mass of Epoxy (g/mol)	Mixing ratio (wt/wt) [(c)]	Viscosity (initial) (Pa.s)	
Commercial epoxy resins	Epolam epoxy 2040+	-	-	3.12:1	0.28 at 25°C	90
	hardener 2042				0.1 at 40°C	
	Epolam epoxy 2020+	-	-	2.94:1	0.55 at 25°C	80
	hardener 2020					
rigid thermosets from neat epoxy+rigid diamine	*DGEBA* der331+	178	356	04:01	0.01 at 100°C	160
	DETDA					
Reinforced[(d)] resin	*DGEBA* der331+				<0.5 at 60°C	
	DETDA+10 wt% MAM[(d)]					
flexible thermosets from neat epoxy+ flexible diamine	DGEBA der331+D2000	2000	356	0.356:1	<1 at 60°C	-25

DGEBA: Diglycidyl ether of biphenol A; DER331; M=356 g/mol; n= 0.15; IPDA: Isophorone Diamine; D2000 jeffamine: polyoxypropylene diamine; M=2000 g/mol; DETDA: diethyltoluene diamine [25]

[(b)] BPO: Benzoyl Peroxide; initiator of Elium polymerization

[(c)] ratio:epoxy/hardener

[(d)] MAM:PMMA-co-Polybutylacrylate-co-PMMA block copolymer (Arkema), it is used as an impact modifier [31]

Table 2: Resin systems for impregnation: name, molar mass, initial viscosity, Tg of fully cured polymers.

chosen with 3 requirements: i) a low viscosity (<1 Pa.s), ii) a short time for room-temperature impregnation/infusion/infiltration (<10 min) and a RT first cure step, iii) a variable final Tg, iv) no solubility between resin and template.

Table 2 gives the resins characteristics according to current literature or technical data sheets.

Three epoxy/hardener systems (bi-component) were chosen out of two epoxy resins:

- Commercial epoxy laminating and infusion formulations-EPOLAM 2020 and EPOLAM 2040 (Axson);
- A neat diglycidyl ether of bisphenol-A oligomer-DGEBA (DER331, Dow Chemicals), n=0.15, (EEW=186 g/eqn., M=372 g/mol). These epoxy resins were crosslinked with either one of the following hardeners providing a different Tg range of the resulting thermoset (Tg<20°C, Tg ≡ 80-90°C, Tg >120°C) [29,30]:
- A liquid aromatic diamine (high Tg) -DETDA80 (diethyltoluene diamine isomers (77–81% 3,5-diethyltoluene-2,4-diamine and 18–22% 3,5-diethyltoluene-2,6-diamine) [29],
- A liquid aliphatic flexible diamine (low Tg)-polyoxypropylene diamine-Jeffamine D2000 (Lonza),
- A standard commercial hardener EPOLAM 2020 or 2042 (medium Tg) (Axson).

A one-component acrylic liquid resin, mainly based on methyl methacrylate, Elium® (Supplied by Arkema), is selected to provide a thermoplastic polymer foam. Elium is a new infusion system used for nautical and wind turbine blades applications; it is assumed to be recyclable after cure, and thermoformable.

Fabrication process of porous polymers (rigid or flexible foams)

Example of sugar templating:

Step 1: Impregnation (Infiltration, Infusion)

Sugar lumps were used as templates without any preparation; their typical average sizes axbxc (mm) are 27.5x18x12=V=5.94 cm^3, or V=axbxc (mm)=16x16x9.7=2.48 cm^3, either cylinders Φ=17.3 mm e=12.3 mm and V=2.89 cm^3.

Lumps are put in aluminum cups (Figure 3 (left)), the liquid resin is poured around the lumps so that only the bottom is soaked in the resin (resin level reaches a maximum of 1/3 of the lump height). Infusion starts immediately at RT from the bottom to the top of the lump, except for DER331/DETDA system which is heated to 60°. It was checked that there is no dependence on the side on which the sugar lump lies into the resin (all impregnation sides are equivalent as to impregnation time, polymerization, and density). Complete infusion is carried out in a few minutes (<4 min); samples are further left 2 hrs soaking in the resin. All templates are impregnated in the same way.

Step 2: Polymerization

Crosslinking is completed as follows: for EPOLAM systems: 12 hrs at RT+2 hrs at 80°C; for DER331/DETDA: 2 hrs at 80°C+2 hrs at 140°C; for DER331/D2000: 0.5 hr at 60°C+3 hrs at 80°C+2 hrs at 135°C; for Elium: 6 hrs at RT+1 hr at 80°C.

Once cured, the infiltrated and cured sugar lumps were cut on the impregnated edge to separate the surrounding neat thermoset (thanks to a saw) and further polished on each edge by any abrasion technique, respecting the sugar-lump initial dimensions.

Step 3: Template leaching

For sugar and salt, polymer-filled templates were soaked in water under stirring for 24 hrs at RT. With 4 lumps together, a volume of 150 ml of deionized water was used. Lumps were then rinsed twice in renewed water (1 hr each time). Finally, samples were immersed in ethanol (for 1 to 2 hrs); ethanol is poured out and samples are left to dry at RT in air for 1 day. An alternative drying method is 60°C for 2 hrs in an oven. The three step (impregnation, polymerization, extraction and drying) do not affect the overall dimensions of preforms.

For the other templates, extraction is carried out i) in hydrochloric acid (HCl, 12M) for the coral piece and the cow bone for 12 hrs at RT (hydrofluoric acid can be alternatively used for cow bone); ii) in dichloromethane for PLA.

For PLA, a first mild extraction, without modifying the regular canal structure (Figure 2) nor the sample dimensions, is carried out by dipping the resin-filled cubes (10x10x5 mm^3) in dichloromethane for 2 hrs in a stirred flask at RT. They are rinsed with the same solvent (CH_2C_{12}) then with acetone, and dried at RT. These extraction conditions do not extract all PLA filaments and make porous the resin-filled scaffolds on only ¾. PLA filaments are still observed by SEM in the core of cube 2.

Results and Discussion

Validation of a fabrication process for several resins

An infiltration time of less than 4 min is valid and reliable for all preforms and all resin formulations. Chosen resins are suitable for fiber reinforced composites and coatings, and have a sufficient wettability onto the preform pores. Their surface tension is between 36 and 43 mJ/m^2 for epoxy formulations and 30 mJ/m^2 for Elium. Depending on its nature, sugar has a surface energy between 38 and 45 mJ/m^2 while NaCl is over 150 mJ/m^2; thus template surfaces can be wetted. But these monomeric resins do not dissolve the preforms in the time given for infusion and cure. Resins are cured within the template following the same cure cycles as those described for the neat resins and $Tg^{cured\ neat\ polymer}$ is measured.

Dimensions of preforms are preserved after polymerization; the measured density is reproducible between samples.

The same process enables rigid or flexible polymer foams (Tg^{matrix} from -20 to 150°C) with a choice of a long chain amine hardener (e.g D2000). No residual sugar was detected by DSC or TGA after water extraction. However, the total filling of templates may be difficult as it will be shown in the following discussion.

Figure 3 show examples of templates and their porous polymer replications. Samples are shown before impregnation or after (impregnation–polymerization–extraction).

Table 3 gives the measured densities of polymer foams after water extraction of templates. Whatever the polymer matrix and the template, the density of foams lies within a range of 0.25 to 0.40 g/cm^3 (except porous polymers from 3D printed scaffolds), i.e a volume porosity between 65 and 78 vol%, driven by the initial template.

Total void filling by the polymer resin implies that the template voids are replaced by resin so that eqn. (4) should be verified.

$$Xvoid^{template} = \rho porous\ polymer/\rho neat\ polymer \quad (4)$$

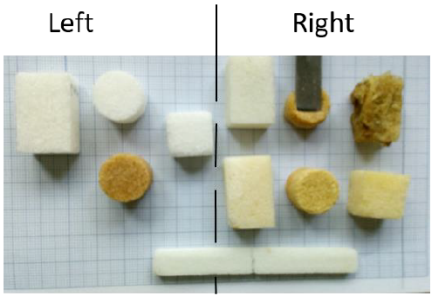


Figure 3: Porous replications from different sugar templates; Left: raw sugar templates before pregnation; Right: Porous polymers from these templates (after sugar extraction).

Polymer type	**Original Template**	**Typical Sample Dimensions** (mm)	**Apparent Density** (g/cm^3) **Porosity** (%)	**"Filling Ratio"** according to eqn. (5)
Epoxy Epolam	NaCl 400 mm	Φ=35 l=10 to 15	0.27 (76%)	0.94
2040-42	60-90 µm		0.26 (77%)	0.90
Epoxy DGEBA	Coral	-	~0.43	-
DER331/D2000				
Epoxy DGEBA	Cow bone	-	~0.50	-
DER331/D2000				
Epoxy Epolam2020	3D-printed scaffold (cubic)	10x10x5	Cube1 0.50 (60%)	1.06
			Cube2 0.63 (45%)	1.03
Epoxy DGEBA	Beet sugar lumps (rectangular)	27x18x12	0.33 ± 0.02	0.87
DER331/DETDA			(72%)	
Epoxy DGEBA	Beet sugar powder (compacted in bars)	Bars: thickness 4 to 10 mm, L 30 to 100 mm	dispersed values 0.28 to 0.43, mean value around 0.30	-
DER331/DETDA				
Epoxy DGEBA	Cane sugar (cylindrical)	*Φ*=17 l=12	0.29 ± 0.015	0.8
DER331/DETDA				
Epoxy DGEBA	Stevia sugar (cubes)	16x16x10	0.29 ± 0.01	0.70
DER331/DETDA				
reinforced epoxy foam=DGEBA	Beet sugar powder (compacted in bars)	Variable [(e)]	0.16 – 0.26	-
DER331/DETDA+5 or 10wt% MAM			Average 0.20	
Epoxy DGEBA	Beet sugar (rectangular)	27x18x12	0.33 ± 0.02	0.85
DER331/D2000				
Epoxy DGEBA	Cane sugar (cylindrical)	*Φ*=17 *l*=12	0.28 ± 0.02	0.75
DER331/D2000				
Epoxy Epolam2020	Beet sugar powder (compacted in bars)	Variable [(e)]	0.28 - 0.42	-
			Average 0.33	
Epoxy Epolam2040-42	Stevia sugar (cube)	16x16x10	0.24 ± 0.04	0.6
	Cane sugar (cube)		0.31 ± 0.03	0.87
Acrylic (Elium)	Beet sugar (rectangular)	27x18x12	0.31 ± 0.02	0.82
Acrylic (Elium)	Cane sugar (cylindrical)	*Φ*=17 *l*=12	0.27 ± 0.02	0.7
Acrylic (Elium)	Stevia sugar (cube)	16x16x10	0.24 ± 0.02	0.6
Acrylic (Elium)	Beet sugar powder (compacted in bars)	Variable [(e)]	0.17–0.32	-
			Average 0.25	
reinforced acrylic foam= +MAM 10wt%	Beet sugar (rectangular)	27x18x12	0.30 ±0.03	0.8

[(e)] Bars: thickness from 4 to 10 mm, length 30 to 100 mm.

Table 3: Characteristics of polymer foams: original template, Dimensions, Measured (apparent) Density, Porosity calculated by eqn. (3), "Filling ratio" as calculated by eqn. (5).

where the density of cured polymers in dense state is taken as 1.15 g/cm^3.

Eqn. (5) defines the 'Filling ratio', proportion of polymer porosity [$\rho_{\text{porous polymer}}/\rho_{\text{neat polymer}}$] to Xvoid$^{\text{template}}$ (template porosity). If impregnation is complete, the filling ratio should be calculated close to one.

$$\text{Filling ratio}=[\rho_{\text{porous polymer}}/\rho_{\text{neat polymer}}]/\text{Xvoid}^{\text{template}} \quad (5)$$

Although infiltration of sugar templates occurs throughout the samples (on heights or thicknesses of 10 to 30 mm), Table 3 shows that the calculated 'Filling ratio' is not always close to unity, indicating a lack of impregnation (of around 10 to 15%, on average). This is due to the complex pore structure of sugar preforms and a limited infiltration

in the smallest pores in our processing conditions (no pressure, no surface preparation, and the use of as-ready templates).

Advantages and drawbacks of the process

Advantages: Advantages are first connected to the simplicity of the process and the access to large foamed panels of resins. All resins which are used for LRI or RTM composite manufacturing offer a variety of polymer foams. Other less reactive monomers can be used and polymerized by heating the preforms.

Secondly, the salt and sugar templates are low cost and nontoxic products (alimentary). Their extraction is carried out easily by immersion in water at room temperature; extraction does not modify the sample dimensions (piece size) or the replicated structure.

Drawbacks: Very low densities (<0.1) seem difficult to reach in this process. The density values stands within a medium range, 0.25-0.40 g/cm^3, i.e. maximum volume porosity up to about 75 vol%.

Only macro cellular structures have been produced. However, an intrinsic difficulty comes from incomplete impregnation of the smallest pores as discussed previously. On-going studies are being carried out to fabricate open cellular polymers of smaller sizes (vacuum assistance).

Morphologies of polymer foams

Figure 4 presents a sugar template surface observed by digital microscopy and reveals a compacted grain morphology, leaving intergranular spaces.

Figures 5-7 present the morphologies of polymer replications (initially sugar templates) observed by either digital microscopy or scanning electron microcopy; all images exhibit macro cellular open-pores. The observed porous structures are indeed complex and highly multi-dimensional; they show various different voids and struts, i.e pores, canals, walls, and even fiber-like struts (Figure 7).

Morphologies of sugars templated foams are quite analogous and do not depend on resin nature. A mean diameter of open pores can be evaluated in the range of hundredths of µm, typically 100 to 500 µm for epoxies or acrylic. Even if infusion is not always totally achieved in our conditions, the polymeric pore structure is the overall replication of the original tortuous template morphology.

In contrast, 3D printed 'PLA' scaffolds are very regular templates (Figure 2). The resulting epoxy foams are also quite regular. Micrographs show holes and canals in a 3D orthogonal porous network (like porous rods). Figure 2 shows the scaffolds at different stages of the process. After PLA printing, the dimensions of the model scaffolds are preserved: Figure 2a(II) shows PLA filaments of thickness 100 µm for cube 1 and 110 µm thickness for cube 2; while spacing is respectively 90-100 µm for cube 1 and 180-200 µm for cube 2.

After polymerization and PLA extraction, the filling ratio is slightly above unity; meaning that PLA is not completely extracted (indeed the DSC thermogram presents a small PLA endothermic melt; and some residual PLA filaments in the core of the cubes are observed by SEM). A longer extraction time or a second extraction would distort the canals and modify the dimensions of the "porous rods" by CH_2Cl_2 swelling of the polymer epoxy network (after several tests, CH_2Cl_2 is the only solvent able to remove PLA at RT).

Even if 3D-printing is a convenient way to build "on demand" regular templates, extraction of PLA is difficult from small canals.

On another side, seemingly oriented pore structures are observed for the coral replicated epoxy foam (Figure 8) and the bone replicated epoxy foam (Figure 9). But void sizes are in the range of several hundredths of µm.

The replication process is validated on rather large foam pieces (400x400 mm^2) (Figure 10) and provides open-cell macro cellular polymers with good mechanical stability using the same polymer matrices as those used for fiber-reinforced composites manufacturing. Furthermore samples based on thermoplastic foams are thermoformable.

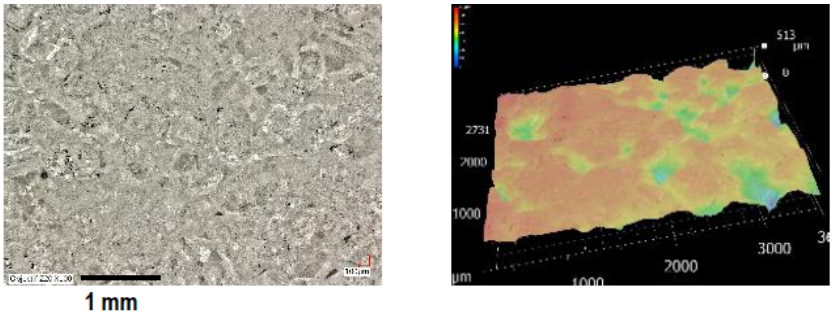


Figure 4: Morphology of a raw sugar template, beet sugar lump, observed by digital microscopy (Keyence VHX5000).

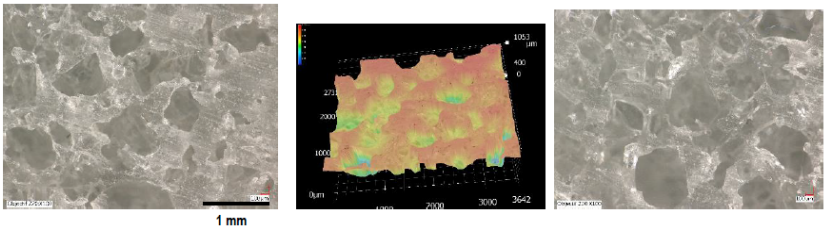


Figure 5: Morphology of a rigid thermoset epoxy foam (Epolam 2040), from beet sugar template (rectangular lump), observed by digital microscopy (Keyence VHX5000).

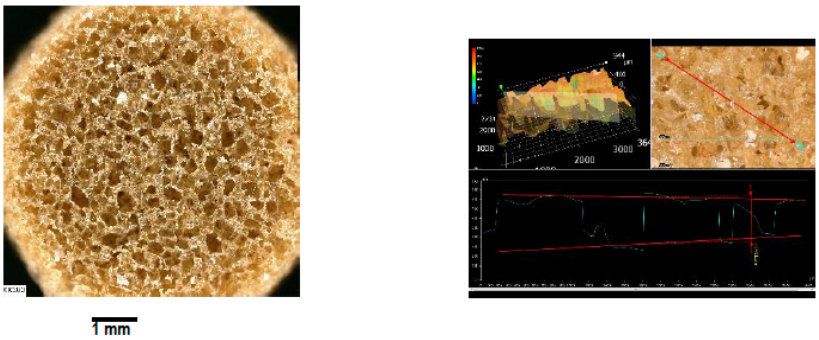


Figure 6: Morphology of a flexible thermoset epoxy foam (hardener D2000), from cane sugar template (cylindrical lump), observed by digital microscopy.

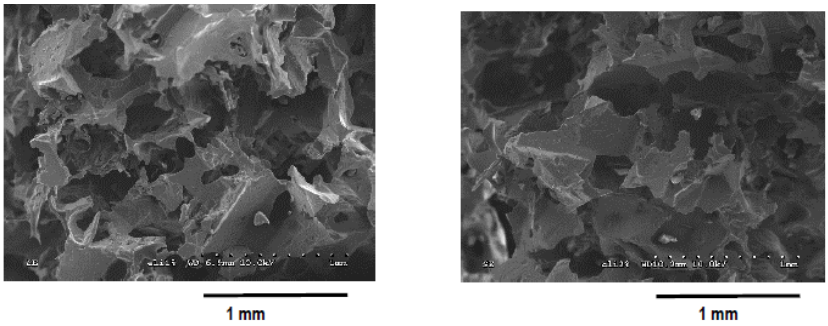


Figure 7: Morphology of acrylic thermoplastic foams (Elium 1, 2 wt% BPO initiator), from beet sugar template (rectangular lump), observed by scanning electron microcopy.

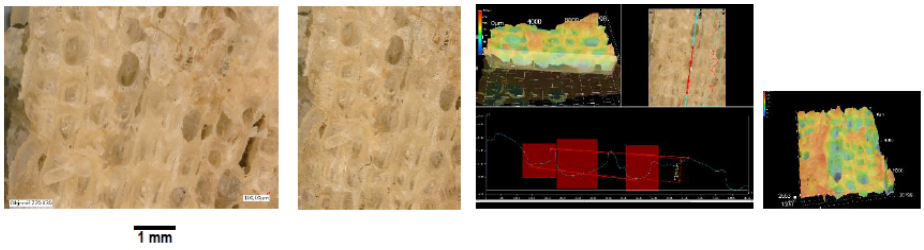


Figure 8: Morphology of a flexible thermoset epoxy foam (hardener D2000), from a coral template, observed by digital microscopy.

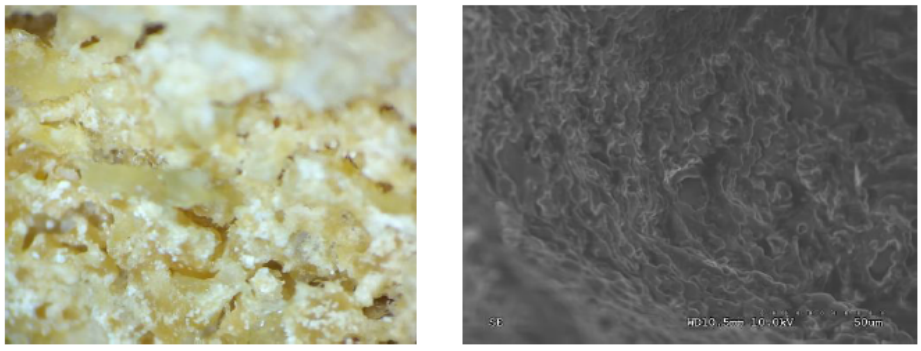


Figure 9: Morphology of a rigid thermoset epoxy foam (Epolam 2020), from a cow bone template, observed by optical microcopy (left) and scanning electron microcopy (right).

Liquid absorption

The foams produced are able to absorb different liquids.

With water, on different sugar-templated epoxies, it is verified that $m^{absorbed}water=Porosity^{epoxy\ foam}$.

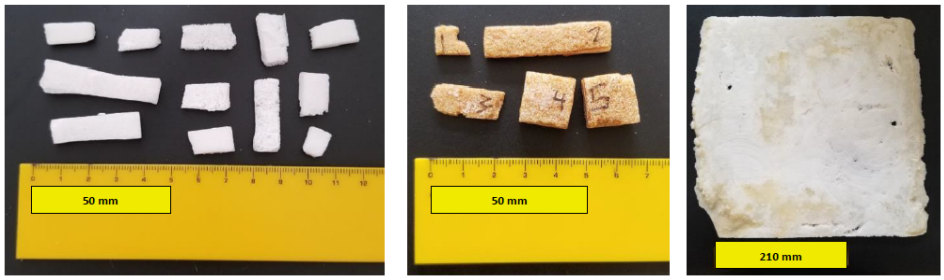


Figure 10: Sugar-templated epoxy and acrylic foams of different sizes and different shapes.

In samples of volume ~25x16x11 mm^3, the total mass of absorbed water is 2.5 to 3 times the mass of foams, in a few minutes (<5 min). So these foams have a sponge-like behavior towards water but also towards other liquids such as ethanol, acetone and silicone oil (density=0.97 g/cm^3), on exactly the same samples.

Potential of the process for the functionalization of fabricated polymer foams

Post functionalization is possible because the epoxy foams do not swell in many liquids and their open morphologies give access to the pores for a reactive liquid. Chemical modification is under investigation, especially *via* the OH functions formed by the epoxy-amine reaction and beared by the crosslinked chains.

Pre functionalized foam is achieved by addition of an additive or a modifier or a nano-filler to the impregnation resin. This possibility exists given that the viscosity is not greatly increased and that the additive is either soluble or stably dispersed during impregnation. Following these lines, the introduction of additives for mechanical reinforcement or electrical conductivity is studied, namely a block copolymer Impact Modifier (IM) or Single Wall Carbon Nanotubes (SWCNT). MAM (methyl methacrylate-co-butylacrylate-co-methyl methacrylate) nanostructured block copolymer [31] was added (10 wt%) to a rigid epoxy foams (DER331/DETDA). Drop tower tests conducted on these foams showed that, in the same testing conditions, sample batch and geometry, DER331/DETDA is brittle while DER331/DETDA-MAM10% shows no break. Results concerning the mechanical reinforcement properties and electrical conductivity will be published in another paper.

Conclusion

We investigated several types of "natural or bio sourced templates" (sugar, salt, bone, coral, PLA 3D-printed scaffolds) for a simple elaboration of macro porous thermoplastic or thermosetting polymers, especially based on resins commonly used in composites manufacturing (e.g RTM-Resin Transfer Molding, LRI-Liquid Resin Infusion). Resin choice (e.g epoxy) may give either rigid or flexible foams, depending on the choice of a hardener molecule. The process consists of 3 simple steps: a) impregnation/infiltration/infusion of the template, b) polymerization of the resin, c) removal of template, mainly by water. It is intended to be easy to handle, robust, low cost, and applicable to many polymer precursors (monomers, oligomers, resins). It is shown that the choice of low viscosity (≤ 0.5 Pa.s at RT), and sufficiently wetting resins (epoxies, acrylates) enables fast impregnation of templates, where impregnation times are <4 min for samples of 10 to 30 mm thickness. The resulting polymeric porous structure, which densities are ranging from 0.25 to 0.4 g/cm^3, is the overall replication of the templates, exhibiting mainly open macro pores in the range of 100 to 500 µm. The detailed morphology is complex and multi-scaled, revealing smaller pores by digital and SEM microcopies. In the chosen 'simple' conditions (room temperature, atmospheric pressure), resin impregnation may be incomplete in the smallest voids, i.e up to 10 to 15 vol% lack of void filling.

This replication process was tested on rather large pieces (400x400 mm^2) and provides open-cell macro cellular polymers with good mechanical stability and thermoformable in the case thermoplastic samples. The foams (without modification) are able to absorb and (re) absorb different types of liquids such as water, ethanol, acetone, silicon oil and hydrocarbons (diesel). The resin filling step is valuable to introduce additives or functions in the foams; e.g an impact modifier was introduced to elaborate improved shock-resistant foams.

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