Editor's Choice

3D Printing of Hierarchical Porous Ceramics for Thermal Insulation and Evaporative Cooling

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Materials for thermal management of buildings offer an attractive approach to reduce energy demands and carbon emissions in the infrastructure sector, but many of the state-of-the-art insulators are still expensive, flammable, or difficult to recycle. Here, a 3D printing process is developed and studied to create hierarchical porous ceramics for thermal insulation and passive cooling using recyclable and widely available clay as raw material. Inks comprising particle-stabilized foams are employed as a template for the generation of the hierarchical porosity. Using foams with optimized rheological properties, the printing parameters and sintering conditions required for the manufacturing of hierarchical porous ceramics via Direct Ink Writing are established. The sintering temperature is found to strongly affect the size distribution of micropores, thus controlling the mechanical, thermal, and evaporative cooling properties of sintered printed structures. By combining suspension- and foam-based inks in a multimaterial printing approach, inexpensive and recyclable clay-based bricks are manufactured with structural, thermal insulating, and passive cooling capabilities.

1. Introduction

Thermal management in residential, commercial, and industrial buildings plays a major role in the ongoing efforts to reduce global energy consumption and greenhouse gas emissions. The building and construction sector accounts for $\approx 40\%$ of the energy consumption worldwide.^[1] In the European Union,

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heating and cooling alone are responsible for half of the total energy usage. Since 66% of this energy is obtained from fossil fuels,^[2] materials for efficient thermal insulation and cooling are considered crucial to lower anthropogenic CO₂ emissions. In addition to deliver the required thermal performance, such materials should also be safe, recyclable, and consume minimum energy during fabrication and operation.

State-of-the-art insulation materials do not yet meet these demands. Polymer-based insulators, such as expanded/extruded polystyrene and polyurethane foams, show relatively low thermal conductivities but suffer from limited fire resistance and endof-life recyclability. Despite the intrinsic fire resistance of inorganic insulators, glass and mineral wools involve high energy processes during manufacturing and exhibit a fiber morphology that is considered hazardous to human health. Aerogels are

attractive inorganic materials for high-performance insulation, but their high cost has so far limited its use to niche applications. The benefits and drawbacks of existing insulation materials provide opportunities for the development of novel technologies.

Porous ceramics have recently received increased attention as alternative insulation materials due to their low cost, fire resistance, recyclability, and relatively low thermal conductivity.^[3–7] Besides thermal insulation, porous ceramics have also been explored to improve the thermal management of buildings by enabling passive cooling of architectural elements.^[8] Passive cooling relies on the evaporation of water infiltrated into the pores of the ceramic, a mechanism that has long been used to lower the temperature of food and water before the advent of vapor compression technologies. Since pores are key structural features required for both thermal insulation and evaporative cooling, the manufacturing of ceramics with controlled porosity holds great potential for the development of energy-efficient technologies for the thermal management of buildings.

In this study, we 3D print hierarchical porous ceramics from wet foam templates and study their thermal insulation and evaporative cooling properties for the thermal management of architectural elements. The hierarchical porous structures are designed to contain a high fraction of macropores that reduce the material's thermal conductivity, while also displaying the micron-sized pores required to enable capillary-driven passive cooling. Using clay as a recyclable, inexpensive, and widely available material resource, we first develop wet foam



Figure 1. Processing steps involved in the manufacturing of hierarchical porous ceramics via extrusion-based 3D printing of wet foams.

formulations with tunable microstructure and rheological properties. The effect of foam rheology and printing parameters on the layer-by-layer manufacturing of 3D structures is then investigated using the extrusion-based Direct Ink Writing technique. Next, we evaluate the microstructure and properties of the hierarchical porous ceramics obtained upon drying and sintering of the printed wet foams. Finally, architectural elements combining structural, thermal insulation, and passive cooling functionalities are 3D printed to demonstrate the potential of these claybased porous materials for thermal management applications in buildings.

2. Results and Discussion

The manufacturing of hierarchical porous ceramics involves three main steps: 1) foaming the suspension of ceramic particles, 2) 3D printing of the stable wet foams, and 3) sintering of the dried printed structures (**Figure 1**). Following this workflow, we fabricate complex-shaped structures that combine the open channels and intricate geometries enabled by 3D printing with the multiscale porosity generated upon sintering of the printed clay-based ceramic.

While the dimensions of the open channels are defined by the programmable print path, the sizes of the pores at smaller length scales are controlled by the foaming and sintering processes (Figure 1). Two classes of pores are formed after drying and sintering of the printed structures. At larger length scales in the range 10–500 μ m, macropores are created from the air bubbles of the initial wet foam. At smaller length scales below 1 μ m, micropores may form within the walls of the macropores as a result of the incomplete sintering of the particles present in the continuous phase of the foam.

The foaming process is crucial to generate the air bubbles that template the macropores and to achieve the rheological properties required for extrusion-based 3D printing. To demonstrate this, we prepare wet foams containing inexpensive and widely available clay as ceramic particles and water as the main liquid phase. Foaming is carried out by mechanically frothing the aqueous suspension of clay particles in the presence of chemical additives that help stabilize the air bubbles.^[9,10] To understand the effect of frothing on the microstructure and rheological properties of the foam, we evaluated the amount of air, the bubble size, and the viscoelastic behavior of samples subjected to different mixing times (**Figure 2**).

Our experiments show that the amount of air incorporated in a suspension with 20 wt.% clay increases quickly from 20% to ~80% within the first 30 sec of the frothing process (Figure 2B). Further mixing up to 7 min does not change the level of air introduced in the foam. This air content compares well with that of mechanically frothed foams studied in previous research.^[3,11] In contrast to the constant air content, the size of the incorporated air bubbles was found to steadily decrease from 109 to 70 μ m as the mixing time increased from 30 sec to 6 min (Figure 2B). This microstructural change was accompanied by a strong shift in the rheological properties of the system, which transformed from a fluid suspension to a viscoelastic foam.

To quantify this marked change in rheological properties, we performed oscillatory shear measurements on foams prepared for mixing times varying within the range 0.5–4 min (Figure 2D). The results show that all evaluated foams display viscoelastic properties, with a storage modulus (*G*') higher than the loss modulus (*G*'') at low shear strains and a well-defined cross-over between these values at a critical shear stress. We take the critical cross-over value as the yield stress (τ_p) of the wet foam. Our rheological experiments show that a four-fold and a threefold increase in yield stress and storage modulus, respectively, is observed when the mixing time increases from 30 sec to 4 min (Figure 2E).

The interplay between foam microstructure and rheological properties explains the experimental observations described above. The increase in foam stiffness and strength with mixing time can be attributed to the formation of an elastic network of progressively smaller air bubbles. Because of the lower deformability and ability to form a network with higher density of inter-bubble connections, small bubbles often lead to foams and emulsions with higher yield stress and storage modulus.^[12–14] In turn, the increase in yield stress with mixing time enhances the shear forces exerted on the air bubbles, favoring their rupture into smaller units during frothing.^[11] These positive reinforcing effects proceed until the foam becomes too stiff and brittle, thus undergoing fracture before shear-induced bubble rupturing can take place. Under this extreme condition, bubbles coalesce and the yield stress drops (Figure 2B,D).

Control over the rheological behavior of the wet foam is crucial for 3D printing of complex-shaped structures. The high www.advancedsciencenews.com



Figure 2. Microstructure and rheology of clay-based wet foams. A) Schematics illustrating the preparation of the wet foam by mechanically frothing an aqueous suspension containing clay particles and a foaming agent. B) Air content and average bubble size of foams as a function of the mixing time. C) Digital optical microscopy images showing the microstructural changes of the wet foam with increasing foaming time (scale bars: 500 μ m). D) The storage (*G'*, filled symbols) and the loss (*G''*, empty symbols) moduli as a function of the stress amplitude for 20 wt.% clay suspensions prepared by mixing for 30 s, 2 min, and 4 min. E) Dependence of the yield stress and low-strain storage modulus of the wet foam on the mixing time. Filled circles depict the measured yield stress, τ_{γ} , and empty circles the storage modulus, *G'*.

yield stress and low density of the foam enables 3D printing of grid-like and highly profiled structures without undergoing gravity-driven distortions. While this is highly beneficial for large-scale applications, the compressibility and viscoplastic behavior of the foam introduce another challenge during 3D printing. Because of their compressible nature, wet foams may show flow instabilities in the form of stick-spurt behavior when extruded at a constant nominal flow rate.^[15] This leads to discontinuous extrusion of the material, which is ejected in periodic spurts rather than smoothly deposited as a new continuous layer (Video S1, Supporting Information). To study this effect and identify strategies to achieve stable printing, we performed systematic extrusion experiments with foams displaying a broad yield stress range (**Figure 3**).

Printing experiments conducted on a wet foam of fixed composition and yield stress show that the extrusion process occurs through different regimes depending on the applied nominal flow rate, Q_i (Figure 3). In these tests, the pressure applied to the ink (ΔP) and the effective flow rate (Q_{eff}) were measured while keeping the nominal flow rate constant. The experiments showed that the wet foam requires a minimum yield pressure (ΔP_{y}) in order to initiate flow. Overall, the ΔP_y values



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Figure 3. Printing behavior of clay-based wet foams. A) (Left) Schematics showing the extrusion-based printing setup and the parameters controlling the imposed (Q_{ij}) and effective (Q_{eff}) flow rates under constant volumetric displacement conditions. *F* is the printhead velocity, h_N is the print height, d_N is the nominal diameter of the print line, u_i is the imposed velocity of the piston (constant), and *A* indicates the relevant cross-sectional areas. (Right) Experimental extrusion map depicting three distinct regions depending on the yield pressure of the foam (ΔP_{γ}) and the imposed flow rate (Q_i) : liquid phase migration (blue), stick-spurt instability (red), and stable printing (green). The critical flow rates $(Q_{i,c})$ needed to overcome the stick-spurt instability is indicated by the yellow points for different foams. The dashed line represents the linear fitting used to calculate the dimensionless value, W_c . B) Pressure drop evolution ΔP and effective flow rate Q_{eff} along the printing line for conditions representing the three different regions in (A). The effective flow rate was estimated by image analysis of the photographs of the printing lines. The nozzle diameter was 1.6 mm and the nozzle height was 4.5 mm in each case. Printing speeds *F* (from 1 to 3): 5.2, 15.7, and 62.9 mm s⁻¹.

of individual foams were found to correlate well with the yield stress levels (τ_{γ}) obtained under shear conditions. Because they directly express the forces needed for extrusion, the ΔP_{γ} values were used to characterize the different rate-dependent flow regimes of the foam in an experimental extrusion map (Figure 3A).

At very low Q_i values, we observe the phenomenon of liquid phase migration, in which part of the particles and air bubbles are retained in the nozzle tip while the continuous aqueous phase drips onto the substrate (Video S2, Supporting Information). This general phenomenon usually takes place in emulsions, foams and suspensions when the viscosity of the continuous liquid is not sufficient to uniformly displace the dispersed phase.^[16,17] By increasing the nominal flow rate above 2 mL min⁻¹, the extrusion regime changes to the stick-spurt mode, resulting in the formation of periodic beads of spurted material along the print path (Figure 3B, mode 1). The stickspurt instability is reflected in the large fluctuations in pressure and effective flow rate of the ink. If the flow rate is further increased beyond a critical threshold value ($Q_{i,c}$), the extrusion process switches to a continuous deposition mode after an initial overshooting. This enables the formation of a uniform and uninterrupted print line (Figure 3B, mode 3) under a stable printing process at relatively constant pressure and effective flow rate. To print 3D structures with high fidelity it is therefore desired to extrude the foam at a flow rate above the critical value, $Q_{i,c}$. Interestingly, our experiments reveal that these critical values increase with the yield pressure (ΔP_{γ}) of the foam (Figure 3A).

To better understand the observed correlation between the critical flow rate $(Q_{i,c})$ and the yield pressure of the foam (ΔP_{γ}) , we theoretically analyze the response of the compressible foam to the imposed volumetric displacement following earlier work on the extrusion of chocolate.^[15] In this analysis, the foam is expected to first be compressed by the displacing piston until the yield pressure is reached. Once the pressure level surpasses ΔP_{γ} , the foam accelerates within the extrusion chamber toward the nozzle tip. At the critical flow rate $(Q_{i,c})$, the timescale for

acceleration is comparable to the timescale needed for full compression of the foam. The ratio between the inertial and compression timescales can be expressed by the dimensionless number: $W = (k\rho Q_i^2)/(\chi \Delta P_v^2)$, where ρ is the foam density, χ is the foam compressibility, and k is a geometrical parameter that depends on the effective length (L_{eff}) , radius (R) and volume (V) of the extruding chamber (see Figure S1, Supporting Information).

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Previous theoretical analysis has shown that the stick-spurt phenomenon can be prevented by imposing a nominal flow rate above the critical value $(Q_{i,c})$. Translated in terms of the dimensionless number above, this means that stable printing occurs when $W \ge W_c$. For the critical condition, we should then expect the nominal flow rate to vary with the yield pressure as follows: $Q_{i,c} = (\pi R^2 V \chi W_c / (\rho L_{eff}))^{1/2} \Delta P_{\gamma}$. Earlier experiments on the cold extrusion of milk chocolate indicate that stick-spurt phenomenon is observed for $W = 3.00 \times 10^{-9}$, whereas a W value of 1.86 \times 10⁻⁶ results in stable, uniform extrusion.^[15]

The linear dependence between $Q_{i,c}$ and ΔP_{v} predicted by the above equation is in good agreement with our experimental data at the critical condition (Figure 3A). To determine W_c , we fit a linear equation to the experimental $Q_{i,c} - \Delta P_y$ data and assume the obtained slope (α) to be equal to $(\pi R^2 V \chi W_c / (\rho L_{eff}))^{1/2}$. Taking available experimental data for R, V, χ , ρ , and L_{eff} , we estimate a W_c value of 3×10^{-7} for the clay-based wet foams prepared in this work (see Supporting Information). This W_c value lies in between the values previously reported for the unstable and stable extrusion of chocolate, suggesting that our quantitative analysis captures reasonably well the physics of the printing process.

The theoretical analysis and the extrusion map obtained allows us to adjust the printing parameters according to the rheological properties of the compressible ink, so as to ensure the stable extrusion of the wet foam into complex-shaped 3D structures. We illustrate this by printing a twisted profiled object with a pentagon-shaped cross-section using a foamed ink with a yield stress of 740 Pa (Figure 4). The applied nominal flow rate of 30 mL min⁻¹ ensures continuous deposition of the foam filaments, whereas the yield stress of the foam prevents distortions induced by gravitational and capillary forces.^[18,19]

To create a hierarchical porous ceramic, the printed foam is dried at room temperature for 72 h and afterwards sintered in an electrical oven at temperatures in the range 1000-1150 °C. Drying removes the liquid phase of the foam, whereas



Figure 4. Microstructure and properties of hierarchical porous ceramics. A) Digital photograph of hierarchical porous structure obtained after drying and sintering of printed wet foams. Scale bar: 1 cm. B,C) SEM images of sintered porous structures generated from a wet foam containing 35 wt.% clay in the continuous aqueous phase. The foams were sintered at either B) 1000 °C (2 h, yellow frame) or C) 1150 °C (1 h, brown frame). Scale bars: 100 µm (left) and 2 µm (right). D) Thermal conductivity, E) compressive strength, and F) Pore size distribution of structures sintered at 1000 °C or 1150 °C. The concentration of clay particles used in the initial aqueous suspension is indicated in the legends. The total porosity of the structures is shown in (D). G) Wicking behavior of selected porous structures, displaying the time evolution of the wet front height, h_{w} . Fitting curves using Washburn's model are represented as dashed lines.

sintering leads to the densification and formation of strong bonds between the clay particles. By strengthening the interparticle connections, the sintering step significantly increases the mechanical stability of the printed object, allowing for easy handling and manipulation. Because of the densification of the assembly of particles around the air bubbles, the drying and sintering processes are accompanied by a linear shrinkage of approximately 8 and 3–15%, respectively.

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The microstructure of the sintered object contains macropores and micropores that reflect the morphology and composition of the initial particle-laden wet foam (Figure 4). We show this correlation by characterizing the pore size and porosity of objects obtained from wet foams containing 20 or 35 wt.% clay particles and sintered at either 1000 or 1150 °C. At larger length scales, the macropores were found to be comparable in size and morphology to the air bubbles of the initial templating foam (Figure 4B). At smaller scales, micropores are formed on the walls of the macropores because the network of clay particles is not fully densified during sintering. The volume and size distribution of micropores depend on the sintering temperature and particle concentration in the initial foam. For a particle content of 35 wt.%, surface area analysis (BET) indicates that specimens sintered at 1150 °C show a family of micropores with average diameter of 5 nm. If the sintering temperature is lowered to 1000 °C, the 5 nm pores are accompanied by a large fraction of pores between 20 and 80 nm. Interestingly, the 20-80 nm pores are also formed when the sintering temperature is kept at 1000 °C and the initial particle concentration is reduced from 35 to 20 wt.%.

The ability to tune the microporosity using the sintering temperature and particle concentration opens the possibility to control the overall porosity, mechanical properties and thermal conductivity of the porous ceramic (Figure 4D,E). Using these control parameters, we produced objects with overall porosity ranging from 90% to 97%. The overall porosity directly affects the mechanical and thermal properties of the sintered material, which display the well-known trade-off reported in previous studies.^[3,4] Samples with porosity in the range 93–97% show low thermal conductivity values of 44–37 mW K⁻¹, which is comparable to those of the best-performing non-flammable thermal insulators.^[6,20] However, this comes at the cost of a relatively low compressive strength of 0.07-0.17 MPa. Notably, if the overall porosity is reduced to 90%, we find that the compressive strength increases by one order of magnitude. This strengthening effect is accompanied by a relatively mild loss in thermal insulation performance, as indicated by the 1.6 fold increase in thermal conductivity. Such favorable balance between mechanical and thermal properties can be attributed to the removal of the strength-critical 20-80 nm micropores from the macropore walls while keeping a high overall porosity in the structure.

In addition to controlling thermal and mechanical properties, the micropores of the hierarchical porous ceramic can also be exploited to enable passive cooling of the structure. Such functionality is achieved through the capillarity-driven filling of the open micropores with water combined with the steady evaporation of the adsorbed water from the surface of the object. To enable uninterrupted cooling, the rate at which the micropores are filled with water should match the rate of surface evaporation. The evaporation rate is determined by the structure's exposed area, temperature, relative humidity, and the air flow conditions in the surrounding environment. In turn, the water filling rate depends on the wetting behavior of the solid phase, as well as the size distribution and fraction of micropores.

To evaluate the water filling rate of our hierarchical porous structures, we performed wicking experiments on specimens sintered at 1000 and 1150 °C (Figure 4G). In this experiment, the bottom of a dry sample is placed into a water bath and the capillarity-driven rise of water through the structure is measured as a function of time. The obtained data was found to be well described by the Washburn equation, according to which the position of the water front scales with the square root of the elapsed time (see Equation S4, Supporting Information).^[21,22] The water infiltration rate is lower for the specimen sintered at 1150 °C, which likely reflects the smaller pore sizes of this structure. Taking our experimentally measured average pore size of 5 nm and assuming typical literature values for the other relevant parameters, we use Washburn's equation to predict the contact angle of the solid phase of the foam structure (Supporting Information). The value of 10° obtained from the fitting reveals the hydrophilic nature of the sintered clay and is in reasonable agreement with previous work on similar materials.^[23] Under the reasonable assumption that the structure sintered at 1000 °C also displays a contact angle of 10°, we predict the wicking behavior of the samples treated at this lower temperature to be controlled by an equivalent pore size of 14 nm (Supporting Information). This pore size falls within the broad size distribution measured for this structure (Figure 4F), suggesting that our simple analysis properly describes the wicking behavior of our hierarchical porous materials.

The unique thermal, mechanical and wetting properties of the hierarchical porous structure can be harnessed for the 3D printing of low-cost building elements with energy-saving thermal management functionalities. To this end, we propose a thermal management concept in which load-bearing, thermal insulating, and passive cooling capabilities are combined in a printed building element using clay as the single chemical constituent of the entire structure. This uniform chemical composition bricksbricks enables recycling at the end of life of the structure, whereas the hierarchical porous architecture gives rise to the multiple functionalities of the printed bricks.

The envisioned thermal management concept relies on a multifunctional brick module that is able to thermally insulate a building in the cold season and cool it down during warm periods, while also playing a load-bearing mechanical function (**Figure 5**A,B). Two inks are designed to provide such structural and thermal functionalities. For the structural role, we use a suspension-based ink with a high concentration of clay particles that can be dried and sintered into high-strength elements after printing. The thermal functionalities require the hierarchical porous architecture of the objects obtained by printing the foam-based inks.

Thermal insulation is achieved by incorporating the porous hierarchical material into the open space within the structural elements. Passive cooling is possible by printing a channel architecture that allows for the imbibition and evaporation of water within the micropores of the hierarchical structure. A two-channel architecture is designed to enable cooling of the conditioned air in a channel with dry dense walls and evaporation in an adjacent www.advancedsciencenews.com

Heat Transfer Q B C Α Dense Ceramic **Porous Ceramic** Inside Dry channe Porous Ceramic (as thermal insulator) Hot dry air Porous Ceramic (as passive cooler) Outside D G line b line c 2 distance [cm] 4 0 C line Φ 6 18 20 22 24 26 28 Air blowing Air blowing Water bath T [°C] off on

Figure 5. Thermal management concept using hierarchical porous structures for thermal insulation and evaporative cooling. A) Multimaterial 3D printing setup using a commercial robot with two extruders. B) Design and working principle of a multifunctional 3D-printed clay-based evaporative cooling brick. The printed dense clay (brown) has a structural function, whereas the porous structure (white) provides a thermal insulation or cooling function. The principle of indirect evaporative cooling using the porous structure is shown in the section in the dashed box. C) Image of a 3D printed physical prototype of the multimaterial evaporative cooling brick (scale bar 1 cm). D–G) Evaporative cooling experiment using a hierarchical porous structure. G) Vertical temperature profile of the wet specimen without (line b) and with (line c) forced air convection.

channel containing wet porous walls. Such design maintains the cooled air dry, circumventing the typically high relative humidity of air conditioned in single-channel passive coolers.

To prove the envisioned concept, we manufactured 4-cm tall bricks with integrated structural and thermal elements using suspension- and foam-based inks as feedstocks in a multimaterial 3D printer (Figure 5C). By tuning the rheological properties of the two inks, complex architectures with high fidelity could be successfully printed (Video S3, Supporting Information). Preliminary experiments show that large bricks with a similar architecture can be co-sintered to achieve structural and thermal functionalities using clay as single material (Figure S3, Supporting Information). Employing a single material to achieve both structural and thermal functions can potentially reduce the number of different materials used in buildings today. Beyond easier construction logistics, the utilization of fewer materials also improves recycling at the end of life of a building. We expect the recycled ceramic to be re-utilized in different types of products, depending on the microstructure and mechanical strength of the porous material. The more porous and weaker structures sintered at 1000 °C (Figure 4B) require less mechanical energy for grinding and thus can be re-utilized as relatively fine powder for the fabrication of new porous ceramics.^[3] Because of their higher strength and denser wall microstructures (Figure 4C), the materials sintered at 1150 °C can be recycled in the form of coarser particles to be incorporated as "grog" in other ceramic products, such as dense bricks.

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While the structural and thermal insulating functionalities of the bricks emerge directly from the intrinsic mechanical properties and thermal conductivity of the sintered material, the passive cooling effect requires the concerted infiltration and evaporation of water within the micropores of the hierarchical structure. To evaluate whether there is a match between the infiltration and evaporation rates enabled by the microporosity (Figure 5D), we conducted model passive cooling experiments on a hierarchical porous structure partially submerged into a water bath (Figure 5E,F). Cooling was quantified by mapping the surface temperature along the height of the model brick using an infra-red camera.

The experiments show that the evaporation of water from the porous structure enables effective cooling of the infiltrated brick, as evidenced by a temperature drop from 26 to 18–19 °C on the surface of the sample (Figure 5G). The infrared maps indicate that lower temperatures can be reached over a broader surface area if air is blown on the structure to enable forced convection. Under the conditions used in these model experiments, we observed that the cooling effect occurs over a surface area of 56 cm² of the hierarchical porous brick. These results illustrate the feasibility of the proposed thermal management concept as a cost-effective strategy to enhance energy savings in buildings using sustainable and recyclable construction materials.

3. Conclusions

Clay-based hierarchical porous structures for thermal insulation and evaporative cooling of architectural elements can be manufactured by 3D printing wet foams using the Direct Ink Writing approach. The air content, bubble size, and rheological properties of the foam-based inks is controlled by the mixing time during mechanical frothing of an initial suspension of modified clay particles. The yield stress and compressibility of the wet foam leads to a stick-spurt behavior during extrusion using a volumetric-controlled printer. A simple force balance captures the physics of this phenomenon, enabling the prediction of the minimum flow rate needed for continuous deposition of foams with different yield stresses. Drying and sintering of the printed wet foams results in a unique hierarchical structure with 20–130 μ m macropores arising the templating air bubbles and $<2 \ \mu m$ micropores resulting from the partial sintering of the clay particles. The thermal, mechanical, and water absorption properties of such hierarchical structures can be tuned by varying the amount and size of the micropores through the sintering temperature. Structures with a large fraction of macro and micropores show thermal conductivity levels suitable for their use as thermal insulators. The very same hierarchical architecture can also be used for evaporative cooling applications, in which the micropores pull water into the structure via capillary forces while the macropores work as liquid reservoirs. Multimaterial 3D printing of suspension- and foam-based inks enables the manufacturing of architectural elements with combined thermal insulating, evaporative cooling, and structural functionalities. The implementation of these multiple functionalities in a single structure using the same chemistry is a promising route to create next-generation recyclable and sustainable materials for the energy-efficient thermal management of buildings.

4. Experimental Section

Ink Preparation: Inks based on particle-stabilized foams were prepared by first mixing clay powder with deionized water to obtain a 50 wt.% clay

suspension. The clay powder (WM-T, Sibelco, Germany) utilized in such ink features an average particle size $d_{\nu 50}$ of 6 μ m, a specific surface area of 15.8 m² g⁻¹, and a density of 2.65 g cm⁻³. The particle size distribution of the clay powder was measured using a laser particle size analyzer (Partica LA-950, Horiba, Munich, Germany), whereas the density was determined by means of a nitrogen pycnometer (Ultrapycnometer 1000, Quantachrome). Nitrogen gas sorption measurements (Autosorb iQ, Quantachrome) were performed to measure the specific surface area of the clay.

The additives necessary for the preparation of the wet foams were provided by FenX AG and were added to the suspension dropwise until the clay content was reduced from 50 wt.% to 20 or 35 wt.%. In the case of 35 wt.% suspensions, glycerol was used as co-solvent to slow down the drying process. The glycerol replaced up to 20 wt.% of the water used in the formulation. The suspensions were foamed by mechanical frothing for 30 sec, 2, 3, 4, 5, 6, or 7 min. Depending on the batch size, a smaller (Multimix 5, 350W, Braun) or a larger (KMM020, 800 W, Kenwood) kitchen mixer was used. During the foaming process the viscosity rises significantly, leading to large air inclusions in the foam. Such large air inclusions were removed by gently shearing the foam in a speed mixer (DAC 150.1 FV-K, SpeedMixer, UK) at 600 rpm for 15 sec.

Inks based on colloidal suspensions were prepared by hydrating a clay body (Red low fire clay 103, Standard, USA) overnight until a water content of 33 wt.% was reached.

Characterization of the Wet Foams and Colloidal Suspensions: The density of the colloidal suspensions and of the wet foams were determined by weighing a known volume of the inks in a laboratory scale. A 3 mL pipette and a 30 × 30-mm Plexiglas cylinder were used as reference volumes in these measurements. Measuring errors were estimated by calculating the standard deviation of at least three data points and typically amounted to 0.2% and 2% for the pipette and cylinder, respectively. The air content of foams was calculated by applying the equation: Air content = $1 - \frac{\rho_{foam}}{\rho_{theor}}$, where ρ_{foam} is the measured density of the foam and ρ_{theor} is the calculated density of the continuous phase (foam or suspension). For wet foams, ρ_{theor} corresponds to the density of the slurry, while for dried foams it is the nominal density of the clay as estimated by nitrogen pycnometry.

To evaluate the effect of the foaming time on the bubble size, wet foams were spread on a glass slide and imaged with an inverted digital microscope in reflection mode (VHX 6000 with VH-K20 attachment, Keyence). The reported bubble sizes and their standard deviation were extracted from the average bubble sizes taken in multiple images covering an area of at least 8 mm².

The rheological behaviour of the prepared inks was investigated using a strain- and stress-controlled rheometer (MCR 302, Anton Paar) using a Couette geometry for the colloidal suspensions and a 4-bladed Vane geometry for the wet foams. Amplitude sweep experiments were performed at a constant frequency of 10 rad s⁻¹ by increasing the amplitude of the applied oscillatory shear strain from 0.0001% to 1000%. The apparent yield point τ_{γ} of the suspensions and foams was taken from the intersection of the storage and the loss moduli obtained from these oscillatory measurements.

Characterization of the Stick-Spurt Instability: Systematic experiments to explore the printability window of the clay-based foams were performed using a small-scale volume-controlled printer (customized Ultimaker 2+). Print lines with nominal flow rates ranging from 1 to 100 mL min⁻¹ were printed with a conical 1.60 mm nozzle at a layer height h_N of 4.5 mm. The print head speed *F* was adjusted to deposit a line with a fixed nominal diameter of 4.5 mm. The effective flow rates Q_{eff} were estimated by image analysis of digital images of the print lines. The area of the print lines *A* was measured setting a sampling grid $\Delta \gamma$ of 0.9 mm along the line.

 $\label{eq:effective flow rates were then calculated with the following equation:$

 $Q_{\text{eff}} = \frac{F \cdot A \cdot h_N}{\Delta \gamma}$. In this analysis, the shape of the filament was assumed

to be a slab with constant height h_N . The pressure during extrusion was measured by a custom-made pressure sensor. The sensor was kindly provided by Stefan Gstöhl^[24] and was mounted just before the nozzle.

Multimaterial 3D Printing: Large-scale multimaterial printing was performed using a custom-made volume-controlled print head mounted



on a 6-axis robot (IRB 4400 Foundry Plus, ABB). Demonstration pieces of dimensions $380 \times 90 \times 40 \ \text{mm}^3$ were printed at speeds between 22.5 and 35 mm s^-1 while keeping the layer height fixed at 2 mm. Nozzles of 2.8 and 6.3 mm were used for the wet foam and for the colloidal suspension, respectively.

Drying and Sintering of Printed Structures: The printed pieces were dried under high humidity (>70%) at room temperature for at least 1 day (max 4 days) depending on the sample size and composition. To allow for more homogeneous drying, foam casts (150 \times 100 \times 25 mm³ and $150 \times 100 \times 40$ mm³) were dried on a 100 μ m Nylon mesh supported by a metal grid at ambient conditions for at least 2 days. All dried samples were transferred to a setter plate and fired in an electrical furnace (HT 08/17. Nabertherm, Lilienthal, Germany) according to a multi-step heating schedule. The heat treatment comprised a burnout period (200 °C for 2 h, 290 °C for 2 h, and 400 °C for 1 h) and a sintering period (1000 °C for 2 h). The heating rate was 1 °C min⁻¹ for the burnout period and 4 °C min⁻¹ for the sintering period. Some samples were subjected to a second firing cycle, in which the burnout period was skipped and a peak sintering temperature of 1150 °C was reached at a heating rate of 5 $^{\circ}$ C min⁻¹ and hold for 1 h. The cooling rate was uncontrolled in all cases.

Characterization of Sintered Foams: The microstructure of clay samples was characterized using a scanning electron microscope (SEM, LEO 1530, Zeiss GmbH, Germany) at a working distance of 4 mm and an acceleration voltage of 5 kV. Nitrogen gas sorption measurements were performed on a Quantachrome Autosorb iQ instrument at 77 K. Prior to the measurements, the samples were outgassed at 100 °C for at least 18 h. The surface area was evaluated by the Brunauer–Emmett–Teller (BET) method. The pore size distribution was determined by a density functional theory (DFT) analysis using a Non Local DFT (NLDFT) calculation model for nitrogen at 77 K on cylindrical pores in silica. Additionally, the foam densities were calculated by simple geometrical considerations. The porosity of the foams was determined from the foam bulk density ρ_{foam} and the density of the continuous phase as estimated from the pycnometer ρ_{pyc} using the following equation:

$$Porosity = 1 - \frac{\rho_{foam}}{\rho_{pyc}}$$
(1)

The wicking behaviour of the sintered foams was investigated using $85 \times 25 \times 18 \text{ mm}^3$ sized samples, which were cut from one large cast brick using a band saw and levelled out using abrasive paper. One representative sample was used for all reported wicking tests. The sample was held with a clamp and immersed to $\approx 3 \text{ mm}$ into deionized water. Evaporation was minimized by placing the setup into a custommade Plexiglas cell and covering it with a plastic foil. The advancing wetting front h_w was tracked by imaging the sample every 30 sec for at least 2 h. Infrared images of the dry and wet samples were taken with an IR-camera (testo 885, Testo Ltd., UK) both with and without air blowing on the specimen.

The thermal conductivity of foams with different microstructures was measured using a heat flow meter (FOX200, TA Instruments, USA). Measurements were conducted holding the cooler plate at 10 °C and the warmer plate at 25 °C, resulting in an average temperature of 22.5 °C.

Compression tests were performed with a universal testing machine (AGS-X, 1 kN loading cell, Shimadzu). For every formulation, three specimens of approximate size $17.5 \times 22 \times 12$ mm³ were tested. The cross-head speed was chosen to be 10% of the specimen's height per minute. The compressive strength and the compressive modulus were determined by averaging the three obtained values.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

Alessandro Dutto, Michele Zanini, Etienne Jeoffroy, Elena Tervoort, and André R. Studart are cofounders of the company FenX AG, which develops insulating mineral foams.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

additive manufacturing, construction, clay, direct ink writing, porosity

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