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Hierarchically porous composites fabricated by hydrogel templating and viscous trapping techniques

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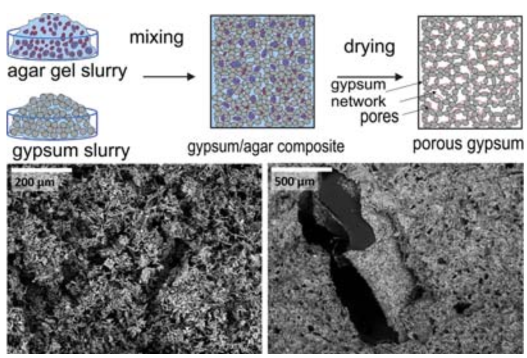
HIGHLIGHTS

- A hydrogel templating technique was used to prepare hierarchically porous gypsum composites.
- A viscous methylcellulose solution was also used to prepare porous gypsum composites.
- These methods allowed for control over porosity and pore size distributions.
- The thermal conductivity was sensitive to porosity but not pore size distributions.
- The mechanical properties were sensitive to porosity and pore size distributions.

GRAPHICAL ABSTRACT



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ABSTRACT

Two methods for the preparation of hierarchically porous composites have been developed and explored. The first involved templating mixed slurries of hydrogel beads with two different average bead size distributions with gypsum slurry which allows for precise control over the porosity, pore size distributions and hierarchical microstructure of the hardened composite after the evaporation of the water from the hydrogel beads. The other technique utilised the viscosity of methylcellulose solution to suspend gypsum particles as they form an interlocked network. By varying the volume percentage of methylcellulose solution used, it is possible to control the porosity of the dried sample. The mechanical and thermal insulation properties of the composites as a function of both their porosity and pore size were investigated. Both methods demonstrate an inexpensive approach for introducing porosity in gypsum composites which reduces their thermal conductivity, improves their insulation properties and allows economic use of the matrix material whilst controlling their mechanical properties. Such composites allow for tuneable porosity without significantly compromising their strength which could find applications in the building industry as well as structuring of other composites for a variety of consumer products.

1. Introduction

Gypsum based composites are commonly used in buildings as dry walls or ceilings due to their relatively low cost, low thermal conductivity and passive fire resistance. This fire resistance stems from a large

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increase in specific heat capacity during the temperature driven removal of the water of crystallisation [1,2]. One way to further improve the thermal insulating properties of gypsum and to decrease its thermal conductivity, requires pores to be incorporated within the gypsum network. Air has a significantly lower thermal conductivity than a solid phase, therefore incorporating porosity within a material decreases its thermal conductivity. Heat transfer in a porous material is accomplished through a combination of lattice vibrations in the solid phase, conduction through collisions of gas molecules within the pores, through thermal radiation and, if the pore sizes are sufficiently large, convection within the pores [3].

Controlling the thermal and mechanical properties of porous and composite materials is an area of significant interest [4–6]. One group has demonstrated how the inclusion of graphene into a polymeric aerogel can produce materials where the thermal conductivity and compressive stress can be increased by increasing the amount of graphene incorporated within the composite [7]. The same effect has been shown when preparing a composite foam of carbon with graphite filler [8]. Another group has prepared a hierarchically porous composite of carbon with silica nanoparticles incorporated within. They achieved thermal conductivities 98% lower than the non-porous carbon which they attributed to the presence of a mesoporous structure [9]. This leads to the Knudsen effect of decreasing the thermal conductivity of air confined in pores smaller than its mean free path. The presence of the silica nanoparticles also contributed to reducing the thermal conductivity of the composites due to them having a lower thermal conductivity than carbon. Therefore the heat flow through the material avoids these regions thus decreasing the phonon mean free path and increasing phonon scattering [10].

Recently, it has been demonstrated that a cheap, easy and environmentally friendly method of introducing porosity into a material, that also gives a large amount of control over both the porosity and pore size, is using hydrogel bead templates. A hydrogel bead templating technique to produce porous materials has previously been reported that involved the use of gellan or polyacrylamide hydrogel beads as templates to introduce porosity into a variety of materials [11]. By combining slurries of the matrix material and hydrogel beads in controlled volume ratios, followed by subsequent curing and then drying, porous materials were obtained with a porosity controlled by the volume of hydrogel beads used. Furthermore, the average pore size of the composite was determined by the average size of the hydrogel beads used.

Here, this method has been extended further to make hierarchically porous gypsum composites by using agar hydrogel beads of different sizes as the templates. The use of agar hydrogel instead of gellan or polyacrylamide is due to the gelling fraction of agar, agarose, being a non-ionic hydrocolloid that does not interact with calcium ions from the gypsum slurry which allows for better control during the formulation of these composites [12]. Fig. 1A shows schematically the process of hydrogel beads templating for fabrication of porous gypsum composites.

A complementary viscous trapping method for controlling the porosity of gypsum through the use of methylcellulose (MC) solution has also been developed. Mixing gypsum slurry with a viscous MC solution during the gypsum setting process stops the sedimentation of the gypsum particles and allows more time for them to hydrate and interconnect into a continuous network. This method allows for control over the porosity, but the pore size increases with increasing volume of MC solution used due to it essentially expanding the innate porosity of gypsum. Schematics of the viscous trapping method for introducing porosity in gypsum composites are presented in Fig. 1B. Both methods can also be used to introduce hierarchical porosity in cement, ceramics, food, home and personal care products and other composite materials of similar setting process. In the current paper, an investigation into

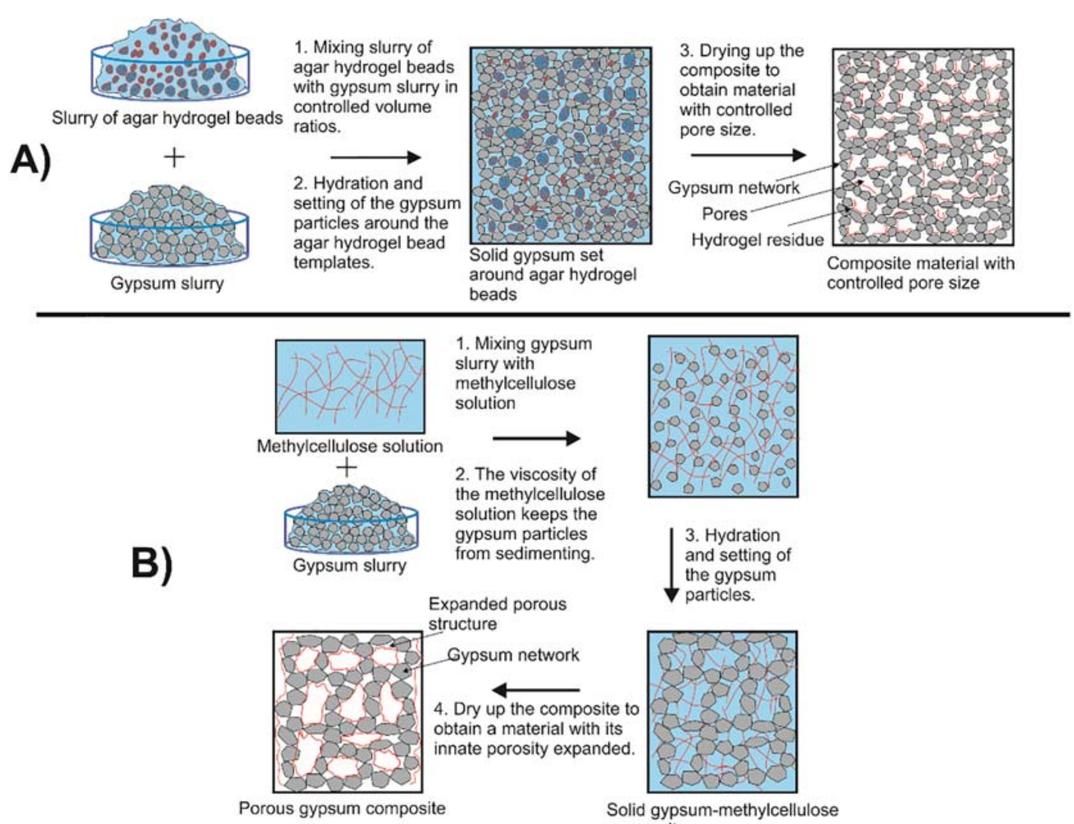

Fig. 1. Schematics to show (A) the hydrogel bead templating technique and (B) utilising MC solution to control the porosity and pore size of gypsum composites. Gypsum slurry is mixed with a slurry of either small hydrogel beads, large hydrogel beads or MC solution in controlled volume ratios. Subsequent setting of the gypsum and then drying of the composite produces materials with controlled porosity and tuneable microstructures.