Nanoencapsulated PCM slurries for the development of thermoregulating gypsums

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Abstract. Gypsums with improved thermal properties have been obtained using a thermoregulatory nanocapsulated slurry (NPCS) as additive. In order to determine the effects of the slurries in the gypsum, physical, mechanical and thermal properties of the different composite materials (gypsum – polystyrene nanoparticles (PS) or nanocapsules (NPCM)) have been studied. Concentrated slurries from polystyrene nanoparticles without (PSS) and with encapsulated phase change material (NPCS) have been synthesized. Firstly, gypsum blocks made of nanoparticles/hemihydrate with mass ratios ranging from 0.0 to 0.42 have been produced from PSS, in order to determine the optimal weight ratio with the best mechanical/physical characteristics. Then, the thermal gypsum block from NPCM/hemihydrate has been prepared at the selected weight ratio. Although PS and NPCM addition reduces the mechanical properties, all the developed materials satisfied the mechanical European regulation EN 13279-2 which limits the mechanical characteristics of gypsums composites. The gypsum composites with PS nanoparticles presented a reduction of the thermal conductivity, so these materials can be used as insulating material. The gypsum composite with NPCM/Hem = 0.3 had an improvement in the thermal storage capacity of 88.76 % and seems to be a good alternative for applying the thermal energy storage technology in buildings.

1. Introduction
It is expected that the world energy consumption will increase a 28 % between 2015 and 2040 [1]. This high and quick growing energy demand can result in depletion of resources, supply difficulties and destructive environmental impact, all these facts are promoting the development and use of sustainable energy resources [1,2]. Solar power is considered one of the most promising renewable energy due to its zero cost, abundance and lack of emissions [3]. However, the intermittency of the solar energy is an important constraint, but the use of thermal energy storage in a building can smooth its temperature fluctuation [4].

Latent heat storage (LHS) is the most studied and promising thermal energy storage technology. The materials used for the LHS are known as phase change materials (PCMs). These materials are able to absorb, store and release energy during the phase change. There are many investigations on PCMs and their applications in thermal energy storage [5]. However, the use of these materials has some limitations. For instance, they must be suitably contained to prevent leakage during the solid-liquid
transition. This leakage can be avoided by the encapsulation of the PCMs into a capsule. In recent years the efforts are focused on obtaining submicron- and nanocapsules, since the smaller the capsules, the higher the surface area, improving the heat transfer [6]. Moreover, these materials can be incorporated in building materials [7].

Up to our knowledge, the use of a highly concentrated polystyrene nanoparticles slurry (PSS) and of a nanoencapsulated PCM slurry (NPCS) to obtain gypsum composites and mainly with thermoregulating properties has not been reported yet. The influence of the PS and NPCM and their content on gypsum thermal, physical and mechanical properties has been compared.

2. Methodology

Gypsum blocks were fabricated by mixing the required amount of hemihydrate (Hem) and slurries, to obtain the mass ratios of nanoparticle/Hem from 0.0 to 0.42 and keeping constant the weight ratio water/Hem equal to 0.6. Then, the rest of the required water was added to the slurry/Hem mixture under vigorous agitation during at least 1 min. After that, the mixture was poured into a mould of 4 cm × 4 cm × 16 cm for preparing the specimens used in the mechanical tests and into a mould of 3 cm × 6 cm × 10 cm for those employed in thermal analysis. Finally, all the specimens were dried under room conditions.

The gypsum blocks have been characterized by measuring their density (ρ), flexural and compressive strengths and their thermal energy storage capacity. The thermal properties have been obtained by putting the gypsum block on an aluminium cell heated by a thermostatic bath, performing a temperature step change from 18 to 40 ºC, recording the input and output heat fluxes and the external temperature. Scanning Electron Microscopy images were carried out in a FEI QUANTA 200 SEM using potentials ranging between 5-30 kV.

3. Findings

All the physical and mechanical tests of the gypsum blocks have been performed following the European regulation EN 13279-2 referred to construction gyspums.

3.1. Physical properties

Figure 1 shows the variation of the apparent and real densities (ρ) and porosity of the gypsum blocks as a function of the different weight ratios of PS/Hem for a constant weight ratio water/Hem of 0.6.

![Figure 1](image_url)

Figure 1. a) Apparent and real densities and porosity of the gypsum blocks versus the weight ratio of PS/Hem. b) SEM images of gypsum composites having different mass ratio PS/Hem mass ratio.

As can be seen in Figure 1a, the apparent and real densities decrease, while the porosity augments linearly, as the ratio PS/Hem is increased. These behaviours are due to the fact that as the proportion of the PS increases, for the same volume of gypsum blocks, their mass is reduced since the polystyrene density is lower than gypsum one and, therefore, there is a decrease in the densities. In Figure 1b, it is possible to observe that porosity increases with increasing mass weight ratio due to the gypsum crystal
separation induced by the incorporation of PS material. Besides, the shape of the crystal is altered by the presence of the polystyrene nanoparticles from elongated prisms to platelet rectangles. It is worthy to point out that the $\rho$ of all the gypsum blocks comply with the European regulation EN 13279-2.

3.2. Mechanical properties
In order to evaluate the effect of the PS/Hem weight ratio on the mechanical properties of the synthesized gypsum blocks, flexural and compressive tests were carried out. Figure 2 shows the results obtained.

Figure 2. a) Flexural strength and b) compressive strength versus the weight ratio PS/Hem.

Figure 2a shows a decrease in the maximum flexural strength as the proportion of PS increases until it becomes practically constant. On contrary in the compression strength essay (Figure 2b) it is observed a sharply decrease in this mechanical property after a PS/Hem mass ratio of 0.3. It is remarkable to say that both of the mechanical tests comply the European regulation EN 13279-2. Thus, attending to the porosity, density and mechanical characteristics, the best gypsum composite containing the polystyrene particles is the one with PS/Hem 0.3, because although the values of its properties diminish respect to the initial one, they are higher enough to agree with the regulations. These results indicate that it is possible to produce gypsum composites with thermoregulating properties containing 0.3 of NPCM per 1 mass of hemihydrate. In that way, a gypsum composite from NPCM and Hem having a mass ration of 0.3 has been manufactured. The results of apparent and real density, flexural and compression strengths were 0.896 g cm$^{-3}$, 1.66 g cm$^{-3}$, 0.478, 4.599 MPa, 6.472 MPa, respectively, whose mechanical properties were higher than the PS/Hem (2.046 MPa, 5.282 MPa for flexural and compression strengths, respectively) with the same mass ratio and practically equal to the unmodified gypsum for the case of the flexural strength (4.866 MPa). The lower depletion in the mechanical properties could be related with the higher mechanical resistance of the shell used in the NPCM respect to PS which is from styrene-DVB instead of single styrene as monomer.

3.3. Thermal properties
Figure 3 shows the external temperature and the accumulative power obtained in each essay. In Figure 3a it can be observed that the slopes of the curves before reaching steady state have a similar appearance, except in the case of the NPCM into gypsum which presents a buffering condition and corresponding with the melting temperature of the PCM. At this condition, the NPCM/gypsum composite absorbs the energy corresponding with the melting of the PCM and avoiding the temperature increase whereas this material continues melting. Furthermore, it can be distinguished that the presence of PS allowed to obtain a lower external temperature, indicating that this material enhance the insulating characteristic of the gypsum. In the same way, the thermoregulating composite presents a lower thermal conductivity at the stationary state than the pristine gypsum. It is distinguished in the Figure 3b that the accumulative power of the pristine gypsum is higher than the PS/gypsum composite confirming the absence of the latent heat storage capacity of the PS material. On contrary, the NPCM/gypsum composite presented a considerably larger accumulative energy (26.535 J g$^{-1}$) in comparison with gypsum blocks (17.721
J g\(^{-1}\)) and achieving an improvement in the thermal storage capacity of 88.76 % from 1.221 to 1.819 J g\(^{-1}\)ºC\(^{-1}\), respectively.

4. Conclusions
It is possible to synthesize gypsum blocks using concentrated polystyrene nanoparticles slurries (PSS) and nanoencapsulated phase change materials slurries (NPCM). It was found that a gypsum composite with mass ratio of 0.3 NPCM/hemihydrate could be manufactured satisfying the mechanical and physical European regulations EN 13279-2. It was observed that the PS and NPCM decreases the thermal conductivity of the gypsum composite whereas the NPCM enlarges the thermoregulating behaviour of the composite, reaching an improvement in the thermal storage capacity of 88.76 %. Thus, by using NPCS it is possible to produce gypsum composites working either insulating or accumulating materials. These properties can be considered as a remarkable achievement to build self-sustaining buildings.

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Figure 3. a) Temperature profiles and b) the accumulative power for manufactured gypsums.