

Encapsulation of Inorganic Phase Change Materials by Sol-Gel Method for Thermal Energy Storage

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Abstract

The macroencapsulation of inorganic phase change materials (PCMs) for eventual application in latent heat thermal energy storage (LHTES) is herewith carried out by a multi-step preparation procedure. These steps are (1) pelletization and sintering (using different granulation techniques); (2) surface treatment (forming an intermediate polymeric layer) and coating via sol-gel method; and (3) final thermal treatment for the densification of the ceramic layer and polymer removal. Effectiveness and reproducibility of each procedure step as well as quality of layers were elucidated by means of Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray spectroscopy (EDX) and mechanical crush tests. Macro-encapsulation procedure was optimized analyzing the thermal performance of capsules by Thermo-Gravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC) and in a conventional oven.

Keywords: Inorganic PCMs, Macro-scale encapsulation, Sol-gel coating, Granulation techniques.

1. Introduction

Latent heat thermal energy storage (LHTES) is one option currently analyzed for concentrating solar power (CSP) plants. The primary features of LHTES lie to its high energy density and capability to operate in isothermal and low pressure conditions. For high-temperature solar thermal applications, phase change materials (PCMs) based on inorganics materials are promising candidates. However, there are some challenges such as the low thermal conductivity, the volume changes during the phase change and the contact surface area, where the effort must focus on the research (Nithyanandam *et al.*, 2016). PCM encapsulation aims at improving the heat transfer between PCM and heat transfer fluid by increasing contact surface. Additionally it serves for two more purposes: (1) it prevents the phase segregation and sedimentation, and (2) it offers a high ratio of area for heat transfer to volume (Alva *et al.*, 2017). Most common encapsulation methods for core-shell PCMs is the sol-gel method, being the only physical method for inorganic materials. Creating an intermediate polymeric layer between the salt and the shell prevents solid salt dissolution during the sol-gel application. On the other hand, an internal void space could provide the expected volume change of the salt, during the heating and melting (Milián *et al.*, 2017).

This work addresses the development of a procedure of encapsulation of inorganic salts shaped in cylindrical pellets on the millimeter-scale, through sol-gel method using dense shells. In order to achieve the best conditions to obtain good quality coatings, different granulations techniques, surface treatments and several ceramic shells have been analyzed. Sodium nitrate and sodium chloride have been retained as representative PCMs, since their melting points (approx. 300 and 800 °C, respectively) are typical temperature ranges in CSP. Titania and silica coatings have been selected to perform the shells. It should be highlighted the potential cost reduction due to the availability of the materials and simplicity of the methods employed in the manufacturing. Customized analysis and experiments have been used to discriminate and to assess the behavior of the products under the working conditions of the aimed application. The characterization methodology employed in this study, which is based on widespread tools used in material research such as SEM-EDX, Dynamometer and TGA/DSC, could become a protocol that allow for comparing researches in the field of the macroencapsulation of PCMs.

2. Experimental

2.1. Sample preparation

The products from the multi-step macroencapsulation procedure are illustrated in Fig. 1, and their preparation was performed as follows:

1. *Pelletization and sintering.* Two granulation methods were used. The first technique is based on a wet method and produces cylindrical pellets with a diameter of 3 mm and with 2 mm of length. In this pelletization, each milled salt was mixed with an additive and water, in a weight ratio of Salt:Additive:Water equal to 10:1:1. As organic binder (OB), oxalic acid (OA) was selected for sodium nitrate and hemicellulose (HC) for sodium chloride. These choices were made taking into account the consistence of the products, being discarded other employed organic compounds. The mixtures were placed in a mold and dried. The second method via dry granulation produces tablets (13 mm of diameter), through which milled salts were compacted under pressure into a mold, using a manual hydraulic press. After pelletization, pellets and tablets were subjected to a first thermal treatment, for the removal of the additive and the sintering of the salt grains. Due to the different physical properties of the salts, the thermal treatment in a conventional oven was specifically designed for each one.
2. *Surface treatment and coating.* Second step for the encapsulation procedure is the sacrificial layer forming, through the impregnation of the agglomerated salt in a solution of polymer (poly-methyl methacrylate or PMMA in benzene). After that, granules were allowed to dry. For the surface treatment, other methods were explored such as the multi-layer forming and also a process of melting the polymer on the substratum. Subsequently, for dense ceramic shell forming two different sols of silica and titania were employed, and after the dip-coated, a drying treatment was included. The process with the coupled steps of immersion-drying, was repeated 3 times obtaining multiple ceramic layers.
3. *Final thermal treatment.* A treatment at higher temperature was performed to densify the film over the substratum, and at the same time, to decompose the polymer.

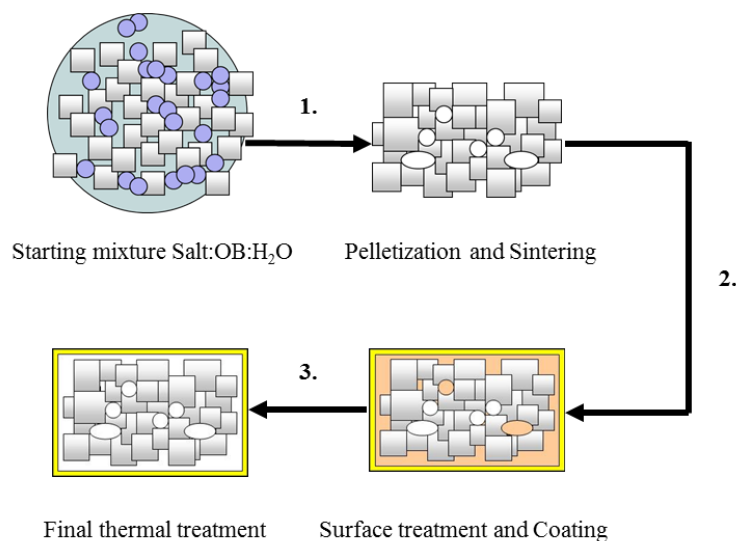


Fig 1. Macroencapsulation procedure.

2.2. Structural and thermal characterization of EPCM

Surface morphology and structure were observed using a scanning electron microscope (SEM) with a TM-1000 Hitachi equipment. This instrument had an energy-dispersive X-ray spectroscopy (EDX) unit, which allows determining the local composition. Samples' volume and density were estimated from the average dimensions and weight of three randomly-chosen samples. Mechanical resistance under compression was studied over the pellets using a dynamometer (Chatillon MT Ametek). Here samples were placed between two parallel plates and subjected to a compressive force until failure and the measurements were performed ten times obtaining the mean value. Designed thermal experiments were used to estimate the thermal resistance of the EPCMs. The first

cyclic test consisted of heating pellets in a conventional oven (Naberthem LHT 02/16 - LHT 08/18 series) in air at $10\text{ }^{\circ}\text{C min}^{-1}$, from room temperature up to $50\text{ }^{\circ}\text{C}$ above the melting point of the salt and the subsequent cooling. This is repeated five times. The phase change properties of coated PCMs were evaluated through a second thermal characterization run in parallel via thermo-gravimetric analysis and differential scanning calorimetry (TGA/DSC). The equipment used was an SDT Q600 by TA Instruments, with a balance sensitivity of $0.1\text{ }\mu\text{g}$ and a calorimetric accuracy of $\pm 2\%$. Measurements were performed using a heating/cooling rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and an air flow rate of 100 mL min^{-1} .

3. Results and discussion

3.1. Optimization of the steps of the encapsulation procedure over tablets

The appearance of the sintered granules is shown on the left side of Figure 2 for NaNO_3 . The wet granulation produces cylindrical pellets 3 mm in diameter and 2 mm in length, of which dimensions vary after the sintering step (Figure 2.a). As can be observed in the SEM micrograph on the right side of Figure 2, the pellets present a rough and porous surface due to the additive removal in the sintering treatment. Figure 2.b) shows tablets, which present 13 mm in diameter, obtained by dry granulation. From micrograph, tablets microstructure seems to be composed of particles of a size smaller than $20\text{ }\mu\text{m}$ connected by the grain boundaries. Tablets possess a more compact structure than pellets and their smooth and flat surface was useful to assess the effectiveness of each step on macroencapsulation using SEM micrographs.

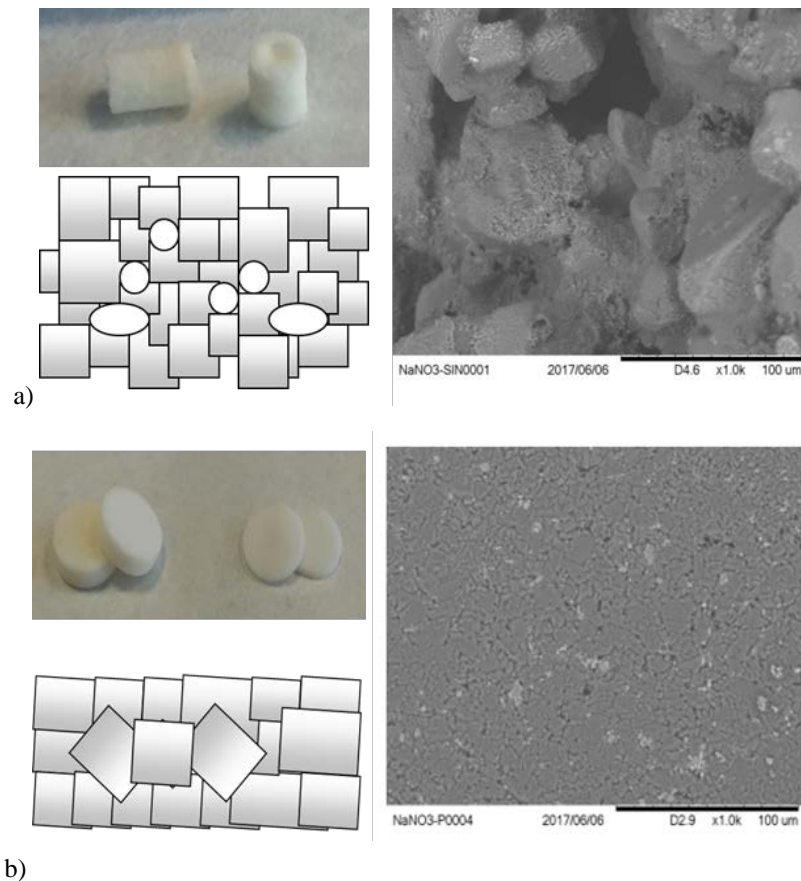


Fig 2. (a) Pellets and (b) tablets made of NaNO_3 .

Thus, after granulation the next step applied is the sacrificial layer forming, made with PMMA. In this point, different methods were explored, obtaining the best surface treatment by applying three consecutive impregnations of tablets in the solution of polymer.

The last step applied for the macroencapsulation procedure is the ceramic shell made of SiO_2 and TiO_2 . To form the capsules over substratum, the treated tablets were immersed into the corresponding sol using the dip-coating technique and a drying treatment was included for solvent removal, obtaining a xerogel. A final thermal treatment

at higher temperature was necessary to be applied in order to densify the metal oxide film over the tablets. In this step, the multiple ceramic coverings were also explored. The micrographs of Figure 3 show the extension of the silica coating when a single or triple layer was deposited over tablets of sodium nitrate. In the single-layer sample, there were some sheets of ceramic material embedded in the salt and the area quantification of silicon element was of 52 wt.%. Although cracked, the metal oxide layer was of a greater coverage when we resorted to the multiple coating, given that Si content achieved 80 wt.% in this zone. Thus, multiple depositions of sols could be considered as the optimized method for the step of the ceramic shell forming. This is a widespread conclusion among all the macroencapsulations performed, regardless of the salt and the sol employed.

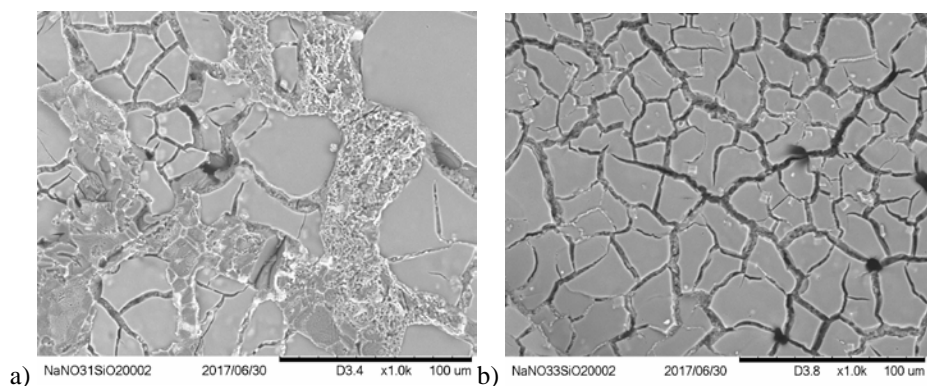


Fig. 3. Tablets of NaNO₃-PMMA-SiO₂ coated with SiO₂. (a) Single and (b) multiple coating.

From the structure analysis of the coatings over nitrate tablets, it can be claimed silica provide better results than the TiO₂ sol taking into account the extension of the metal oxide layers. Titania seems to cover better NaCl surfaces. Regarding the interaction between the polymer layer and the ceramic shells, it was observed that SiO₂ coated better than TiO₂ on surfaces previously covered by PMMA.

Additionally a first assessment on the reproducibility of the procedure showed that careful analysis on synthesis parameters should be performed. Finally, effect of the aging time of sols were also studied and it was confirmed changes on surface morphology using aged sols.

3.2. Appearance and mechanical properties

Once determined the best conditions of the macroencapsulation procedure, these were applied over cylindrical pellets. Appearance, size, density and mechanical strength (resistance) were examined after each macroencapsulation stage, from the wet granulation products to the resulting EPCMs. This characterization allowed for identifying and quantifying how the macroencapsulation stages affect each specimen and their main features are summarized in Table 1.

Table 1. Evolution of the parameters for pellets.

<i>Parameter</i>	<i>Salt/OB/Sol-gel: NaNO₃/OA/SiO₂</i>		
	<i>After Pelletization</i>	<i>After Sintering</i>	<i>After Encapsulation</i>
Color	White	Light yellow	Brown
Structure	Granular	Compact	Wrinkled surface
Volume (cm ³)	0.023	0.022	0.033
Density (g/cm ³)	1.557	1.329	1.370
Resistance (N)	8	19	39
	<i>Salt/OB/Sol-gel: NaCl/HCl/TiO₂</i>		
Color	Light brown	Light grey	Light grey
Structure	Granular	Granular	Granular
Volume (cm ³)	0.018	0.015	0.014
Density (g/cm ³)	1.228	1.229	1.201
Resistance (N)	34	45	69

The sample of NaNO_3 agglomerated with OA, after being taken out from the mold and allowing to dry (Figure 4.a), possesses white and granular homogeneous surface, a well-defined cylindrical shape and mechanical consistency, withstanding a force of 8 N before crush. After OB removing and salt sintering (Figure 4.b), the appearance changes to a more compact and yellowish structure. Density has decreased, and compression resistance has increased. When the triple coat of SiO_2 is densified over pellet (Figure 4.c), volume suffers an expansion (final volume, 33 mm^3), and mechanical properties has been improved much more (final resistance, 39 N), being compared with the initial pellet. A final rough and brown surface suggests color is provided by the components of the gel or the presence of calcination products coming from the organic binder (OA) or from the plastic sacrificial layer.

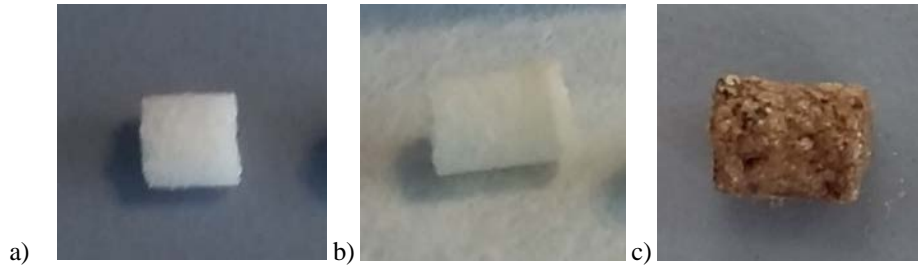


Fig. 4. Evaluation of appearance for the pellets $\text{NaNO}_3/\text{OA}/\text{SiO}_2$.

As Figure 5 shows, the initial sample of NaCl with HC presents a dark color and irregular shape. When the layer of TiO_2 is applied, a sample with a light grey granular structure is obtained. This is the smallest (final volume, 14 mm^3) and least dense pellet, with the highest mechanical properties (final resistance, 69 N).

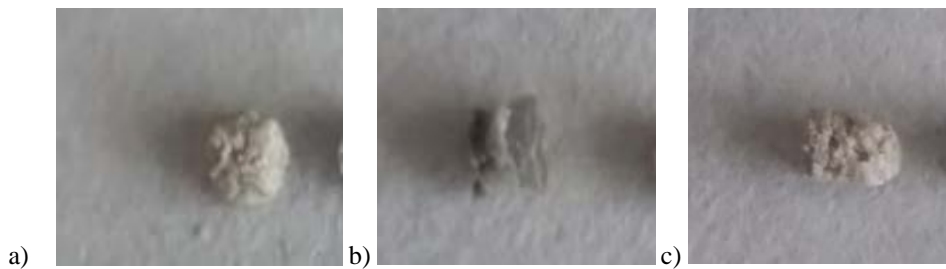


Fig. 5. Evaluation of appearance for the pellets $\text{NaCl}/\text{HC}/\text{TiO}_2$.

3.3. Thermal characterization of the pellets under working conditions

The thermal characterization procedure was described in section 2.2. Thermal tests provide the response of the products in terms of thermal stability for using in storage systems. For NaCl pellets, the maximum testing temperature was $850 \text{ }^\circ\text{C}$. It was observed that the free volume in these products could not be enough to house all the amount of molten salt. In addition, the formed shell could not be dense or sealed enough to overcome the test. Anyway, relative high vapor partial pressure of this salt at the liquid state ($4 \cdot 10^{-4}$ at $801 \text{ }^\circ\text{C}$), causes its vaporization during the successive cycles. NaNO_3 samples could have higher thermal stability because of a lower vapor pressure at the melting point ($1.7 \cdot 10^{-46}$ at $308 \text{ }^\circ\text{C}$). This characterization allowed us to discriminate pellets made of NaCl .

Thermal stability and thermal performance in cycling are both important properties to thermal storage materials. So the second characterization for the capsules was carried out via TGA/DSC. This technique enables to link the latent heat and temperature during the phase change. Figure 6 shows thermogravimetric and calorimetric curves of $\text{NaNO}_3/\text{OA}/\text{SiO}_2$ pellet obtained in $200\text{-}350 \text{ }^\circ\text{C}$ range and for 5 consecutive cycles. DSC results are collected in Table 2.

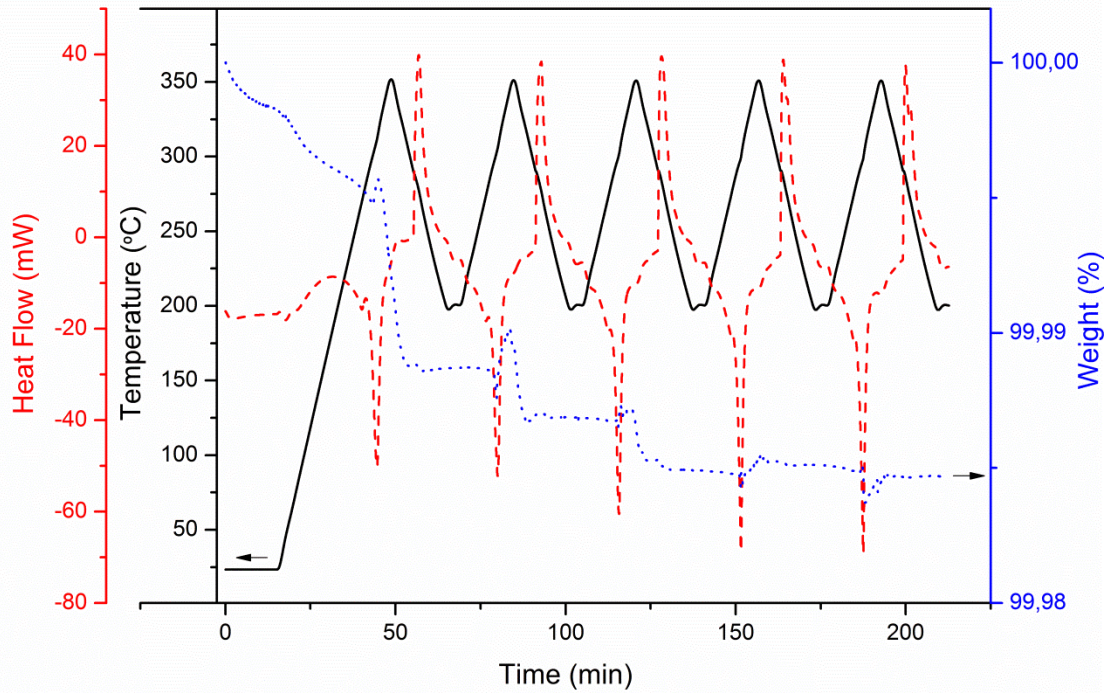


Figure 6. Cyclic TGA/DSC of $\text{NaNO}_3/\text{OA}/\text{SiO}_2$ pellets under dynamic conditions at $10\text{ }^\circ\text{C}/\text{min}$, from 200 to $350\text{ }^\circ\text{C}$ and air flow of 100 ml min^{-1} .

Tab. 2. Calorimetric results of the characterization for $\text{NaNO}_3/\text{OA}/\text{SiO}_2$ pellets.

Cycle	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	T_s ($^\circ\text{C}$)	ΔH_s (J/g)
1	309	113	275	161
2	304	93	277	166
3	301	95	284	172
4	299	99	284	175
5	301	97	288	172

From calorimetric curve (dashed red line in Figure 6), the initial melting peak of NaNO_3 EPCM is located at $309\text{ }^\circ\text{C}$ (T_m). This maximum of rate fluctuates slightly from the second cycle until the end of the run. Thus, mean value of melting point is $303\text{ }^\circ\text{C}$. Regarding the mean value of the latent heat to achieve the liquid state (ΔH_m), it is 99 J g^{-1} . Solidification heat (ΔH_s) could be considered as 169 J g^{-1} , on average. Freezing peak (T_s) is observed at approximately $30\text{ }^\circ\text{C}$ lower than the melting temperature.

On the other hand, TGA/DSC equipment registered simultaneously the changes of the mass while the process was happening. In this case, there is not a considerable loss of mass in each cycle (dotted blue line in Figure 6), where the lost scarce exceeds 1% of the pellet. Thus loss of mass can be considered negligible and TGA/DSC results indicate that $\text{NaNO}_3/\text{OA}/\text{SiO}_2$ pellet exhibits promising capabilities to store thermal energy.

4. Conclusions

A macroencapsulation multi-step procedure was developed for two inorganic salts and applied to produce cylindrical pellets for thermal energy storage in concentrated solar power plants. Encapsulated phase change materials consisted of an inorganic core composed of sodium chloride or sodium nitrate and two concentric layers made of polymethyl methacrylate and silica or titania by sol-gel process, with subsequent removal of the polymer.

Pellets and tablets were obtained through two different granulation methods. Pellets presented rougher and higher

porosity than tablets, so the effectiveness of each macroencapsulation step was initially evaluated and optimized over tablets. These steps were the surface treatment, the drying step for the sol-gel method and the multi-layer ceramic coating. Microstructure of the shells, mechanical properties of pellets, thermal stability and thermal behavior, allowed to select the best coating for each substrate.

NaNO₃ samples with the optimal surface treatment and optimal coating made of SiO₂, presented a better aptitude as phase change material than NaCl core-shell products, for a thermal energy storage system. Thus, the core melting of NaNO₃ EPCMs will allow to work under isothermal conditions and it can help to solve the efficiency problem in solar thermal power plants based on steam/water thermodynamic cycles.

5. References

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