Microencapsulated PCMs for thermal energy storage in the range 300-500 °C: pilot-testing

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Abstract. Phase Change Materials (PCM) became one of the most interesting research directions toward improving the efficiency of concentrated solar power plants. Different methods were proposed to increase storage capacity as a result of the encapsulation protection and efficient thermal energy storage for high operating temperatures. Here, we present a soft chemical process to encapsulate inorganic KNO3 as PCM system using nanostructured ZnO shell material, based on hydrothermal synthesis followed by spray drying and their thermal conductivity measurements are discussed. A unique micro-pilot equipment for the functional characterization of microencapsulated PCMs was designed and built for real time monitoring of thermal properties of these materials.

1. Introduction
One of the main objectives of the European Energy Strategy 2020 is to achieve up to 20% energy savings by 2020. In this context, special attention is given to develop new solutions to increase the energy efficiency. Chemical and thermal energy storage using Phase Change Materials (PCMs) became one of the most interesting research directions toward improving the efficiency of concentrated solar power plants. Potassium nitrate (KNO3) as well as other inorganic salts (NaNO3, LiNO3, eutectics) are commonly used as thermal energy storage materials in Concentrated Solar Plants (CSP) or in processes for waste heat recovering, due to their convenient melting temperature and high latent heat (high energy storage density) [1-6].

Metals are also suitable materials for thermal energy storage but with limited applications due to their higher cost and higher tendency to oxidation compared to inorganic salts. Nevertheless, inorganic salts are also prone to produce corrosion when in contact with the storage reactors, which may also lead to a lack of thermal stability. Therefore, in the last few years, different researches have been carried out to encapsulate inorganic salts into macro (particle size > 1 mm) [7] or microcapsules (μm or nm). Encapsulations consist of a core material (inorganic salt) in a shell or coating material, which avoids the leakage of the inorganic salt and its contact with the container [8].

Other benefits provided by micro-encapsulations include more effective heat transfer due to the increased heat transfer area as well as a faster charging and discharging rates due to the smaller distance during the heat transference [7, 9-10].

Publications focused on the encapsulation of organic PCMs can be easily found in literature. However, studies related to the encapsulations of inorganic PCMs are scarce and published in the last 3-5 years [11-14].
In the case of inorganic salts and KNO₃ in particular, a previous work by the group leaded of M.D. Romero-Sanchez and R.R. Piticescu [15, 16] proposes the microencapsulation of KNO₃ in a ZnO shell by solvothermal process followed by spray drying. The authors have demonstrated that the thermal properties and feasibility of KNO₃/ZnO microparticles as thermal energy storage materials mainly depend on the KNO₃/ZnO ratio and the temperature used during the solvothermal process. It is also worth noting that the thermal stability of the KNO₃/ZnO microparticles is higher for narrow operating temperatures (congruent melting behaviour), as demonstrated by the authors when evaluating heating and cooling enthalpies after a high number of thermal cycles in different temperature ranges by Differential Scanning Calorimetry (DSC) [17].

Not only the energy storage density of the microparticles is important for the greater application in thermal energy storage systems, but a major issue is the thermal conductivity, which should be optimized for a suitable heat charge/discharge rate, avoiding low thermal conductivity values that hampered the heat transference rate, mainly critical for the discharging process. Different studies have been found in literature focused on the incorporation of different high conductive additives or fins [18, 19], but they are mainly based on PCMs with low melting temperature (< 100 ºC) and the ones addressed to high melting temperature are mostly based on numerical studies [20-22].

As a first step and considering the demonstrated efficiency at laboratory scale of KNO₃/ZnO microparticles developed by the authors in a previous work [17], in this study, the feasibility of using this material as PCM in a micro-pilot plant for thermal energy storage has been evaluated both by modelling and experimentally. The pilot plant consists of 1 tank with the novelty of using a sensor to in-situ evaluate the thermal conductivity, which allows to estimate the required thermal conductivity for optimized charging/discharging processes as well as identification of limitations and problems encountered when using KNO₃/ZnO microparticles as thermal energy storage material.

Further work is currently being carried out to enhance the thermal conductivity of the KNO₃/ZnO microparticles by using different conductive particles.

Database collected with the help of the micro-pilot equipment will also be used in new possible applications under development, such as the use of microencapsulated PCMs as cooling system for the thermal barriers / thermal buffers in aeronautics.

2. Experimental methods

Potassium nitrate (KNO₃ p.a. Merck) has been selected as PCM material. For the synthesis of inorganic ZnO matrix to encapsulate the PCM, zinc nitrate hexahydrate (Zn(NO₃)₂ x6H₂O p.a. Merck) was selected as precursor. To avoid dissolution processes of KNO₃ during synthesis (solubility 31.6 g KNO₃/100 ml water), ethylic alcohol (>99.7 vol%, TUNIC Prod. Srl.) was used as reaction media.

A solvothermal method was used for the synthesis of KNO₃ encapsulated in ZnO matrix. In the first step, KNO₃ was dissolved in water and spray dried in a LabPlant system through a 0.5 mm nozzle using a hot air jet at 200 ºC, in order to obtain spherical particles with average sizes <50 μm. Then, the spherical KNO₃ particles were dispersed in ethylic alcohol by mechanical stirring at a concentration of 0.16 g KNO₃/100 ml. The Zn(NO₃)₂ x 6H₂O powder was dissolved in the ethyl alcohol at the desired weight ratio ZnO:KNO₃. The solution pH was adjusted by adding a 3M KNO₃ solution in ethylic alcohol and the suspension was further poured in the Teflon vessel of an autoclave (Berghof, Germany) and treated for 2 h at 200 ºC, under 40 atm Ar pressure. The composite suspension was finally spray dried at 100 ºC in the same LabPlant system using the 0.5 mm nozzle to obtain a white powder with homogenous particle sizes. The procedure is presented in detail in [16, 17].

The chemical composition of the composite powder was analyzed by Inductive Coupled Plasma Spectrometry (Agilent 725 in radial viewed configuration, complete wavelength coverage from 167-785 nm). The phase composition was analyzed by X-Ray diffraction (XRD, Brucker D8 Advance), using the DIFFRAC+ software in the Brag-Brentano method in the θ – θ coupling mode with CuKα radiation source in the angular range 2θ = 4 to 74 º. The thermal properties were measured using Differential Scanning Calorimetry (DSC Netzsch 200 Maya F3) having the working temperature range -40 to 600 ºC. Experiments have been carried out from -20 to 400 ºC with a heating rate of 10
K·min\(^{-1}\). SEM analysis was carried out on a FEI-Quanta 250 System with resolution 3.0 nm, provided with element EDS Analysis system.

To measure the thermal conductivity of the samples, the transient plane heat source (hot disk) method was employed, using the Hot Disk Thermal Constants Analyser (model TPS-2200, from Hot Disk, Sweden). A typical measurement was performed by the apparatus by generating a pulse of electrical current to heat the sensor. Powders with different KNO\(_3\):ZnO ratios were obtained by solvothermal process in ethanol. The powders were poured in a cylindrical shape with 36 mm diameter and 12 mm height and consolidated by thermal treatment in air at 300-310 ºC in an electrical chamber furnace. The time course of the temperature increase response was recorded with the same sensor by sampling the electrical resistance of the heating circuit. The thermal conductivity of the samples was calculated by the instrument’s software.

The values obtained were further used to design a micro-pilot system for real time characterization of the micro-encapsulated PCMs. A first computer simulation to estimate the evolution of temperature profile in the micro-pilot tank with the heating time was done.

3. Results and discussions

In a previous paper [17] we demonstrated that KNO\(_3\) microencapsulated into ZnO shells with the weight ratio KNO\(_3\)-ZnO 3:1 solvothermally obtained at 200 ºC provided the highest stability during more than 20 heating and cooling thermal cycling experiments. The chemical composition according to ICP-OES measurements is: 32.9% K and 20.5% Zn, corresponding to 79.5% KNO\(_3\) and 20.5% ZnO respectively. Figure 1 presents the typical morphology of KNO\(_3\):ZnO composite powders, consisting of ZnO with spherical morphology, which is covering the KNO\(_3\) particles.

![Figure 1. SEM image of the KNO\(_3\):ZnO powder with weight ratio 3:1 (20.5% ZnO).](image)

![Figure 2. DSC curve of the KNO\(_3\):ZnO powder with weight ratio 3:1 (20.5% ZnO).](image)
The DSC diagram of this sample from Figure 2 shows a first peak corresponding to the reversible phase I to phase II transition of KNO$_3$ [23], while the second peak is related to its melting / crystallization process. The enthalpy of melting and crystallization calculated with the help of the DSC Protheus Analysis software are 100.9 J/g and 107.7 J/g, respectively.

The evolution of the thermal conductivity and specific volumetric caloric capacities of samples prepared by solvothermal method vs ZnO content are presented in Figures 3 - 4. One may observe that microencapsulation of KNO$_3$ by the solvothermal method in ethanol leads to an enhancement of the thermal conductivity compared to non-encapsulated PCM, having a value < 0.1 W/mK, with an optimal ZnO content around 25%.

**Figure 3.** Thermal conductivity vs ZnO content in KNO$_3$:ZnO powders obtained by solvothermal process.

**Figure 4.** Specific volumetric caloric capacity vs ZnO content in KNO$_3$:ZnO powders obtained by solvothermal process.

Using the thermal data (melting and crystallization enthalpies, thermal conductivity, specific volumetric caloric capacities) collected for microencapsulated KNO$_3$, a micro-pilot experimental installation was designed and built to study the real functional properties of these materials. The tank filling capacity for KNO$_3$ micro-encapsulated in ZnO is in the range 30-35 kg. The computer
registering temperature profile allows direct determination of the thermal diffusivity of the material filled inside the tank. The thermal conductivity may be calculated using the equation (1).

\[
\lambda(T) = \alpha(T) \cdot c_p(T) \cdot \rho(T)
\]  

(1)

Where \( \lambda \) is the thermal conductivity [W/ m\(^{-1}\)K\(^{-1}\)], \( \alpha \) is the thermal diffusivity [mm\(^2\)s\(^{-1}\)], \( c_p \) is the specific heat [Jg\(^{-1}\)K\(^{-1}\)] and \( \rho \) is the volumetric density [gcm\(^{-3}\)].

The heating system is actually designed to pump high temperature oil stable up to 350 °C but other heating fluids may be further adapted. One main unique feature of the micro-pilot is the possibility to use the hot plate sensor by adapting a special vertical sensor inserted in the PCM material.

As presented in Figure 5, the micro-pilot consists of the following main parts:
The software application is written in C++ language using Visual Studio (version Community 2017) for editing, compilation and debugging and comprise 3 autonomous functional modules: the real time control and visualization module; the thermal parameters computing module; data acquisition, data release and reports elaboration module. The 3 modules are synchronized with the help of a multi-threading model using specific techniques for signal transmission and data storage in buffer memories. A first computer simulation to estimate the evolution of temperature profile inside the micro-pilot tank with the heating time was done.

![Figure 7. Experimental simulation of the thermal storage tank using microencapsulated PCM.](image)

Figure 7 presents the calculated temperature at different z distances from the median axis of the tank when the heating temperature of the thermostat is fixed at the desired temperature 350°C.

4. Conclusions
A solvothermal technology suitable for microencapsulation of KNO₃ (PCM) within ZnO as inorganic shell has been used. KNO₃ particles have been covered by ZnO microcrystals, with thermal properties during KNO₃ transitions similar to those of raw KNO₃ indicating the feasibility of microencapsulated KNO₃-ZnO as PCM for latent heat storage. Microencapsulation in a matrix of 25% ZnO shows that thermal conductivity is enhanced from values < 0.1 W/mK to values over 0.65 W/mK. Beside the size effect of the microencapsulation, the thermal conductivity increase may be explained also by the specific flower-like shape of ZnO micro-crystals [24], but further studies are needed to confirm this assessment. The thermal parameters collected from DSC and hot disk thermal conductivity measurements were used to design and build an innovative micro-pilot equipment to study the functional properties of microencapsulated PCMs in real time conditions.

Experiments are in course to fully start-up and operate the equipment and study different materials as microencapsulating media and thermal energy storage materials for Concentrated Solar Plants and thermal buffering materials in aerospace applications.

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