Incorporation of embedded materials for thermal regulation of buildings

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Construction represents nearly a third of greenhouse gas emissions among industries worldwide. In the context of limiting the consumption of energy to reduce the impact of human activity on environment, this research focuses on the use of materials to improve the properties of thermal regulation of buildings via energy storage.

Phase change materials (PCM) have the ability to store energy within their structure thanks to latent heat during their phase change. In our research, we used materials with solid/liquid phase change at ambient temperature, so it can reach the range of application. Phase change materials represent a wide family of component, and we chose organic ones such as paraffinic as a bystander and fatty acid as biobased compound. Such incorporated PCM inside house wall could help reducing/increasing the temperature from 1 to 4°C during day/night (respectively) "offering" the ability to reduce energy impact of homes (ecologically & financially). Concrete (Portland cement) is also responsible for a huge amount of greenhouse gas, so the strategy was to select geopolymers, known to release up to 60% less CO_2 emissions than concrete during its production. Such study combining multiple concepts can help work on gas emissions and energy efficiency during and after construction.

The main issues were the incorporation of droplets of biobased PCM inside a geopolymer. To overcome them, PCM were encapsulated to avoid leakage and breakage during expansion of the solid-liquid transformation of the PCM. Optical and electronic microscopy, infrared spectroscopy, Laser granulometry, Thermogravimetric analysis and Differential Scanning Calorimetry were used to characterized our experiments. Another alternative to encapsulation is to apply such compounds directly on constructed buildings as a coating agent, enhancing insulating properties of defecting housings.

Keywords (maximum 5): Phase change materials (PCM), biobased PCM, geopolymers, encapsulation, energy storage, Differential Scanning Calorimetry.

Introduction

Renewable energies have gained lots of interest for decades, thus solar energy is really promising to reduce our environmental impact. The problem is that solar energy depends on the moment of the day and seasons, so storage systems can be useful for charging and discharging energy. Among solar energy systems, thermal energy storage is a known technique. This technology is based on the changing state intrinsically linked to the materials. This phenomenon is based on basic thermodynamics indeed, when a material goes from liquid to crystal, energy is released mostly in heat form. Heat can then be used as an advantage for diverse applications. To the contrary, when a material melts, it will need energy to get liquid and one way is to absorb energy under heat form. This promising technology allows the temperature range to be modulated and adjusted to the application [1]. It allows the energy to be stored for several days, months or even seasons.

Among thermal energy storage, one type has grown useful in numerous domains [2]: latent storage. The materials with this ability to store and release energy depending on their initial state are called Phase change materials (PCM). Since 1970, PCM are used in buildings to enhance thermal comfort and as a response to the increase of energy demand of an on growing population. Nowadays, human activities emit more and more greenhouse gas each year, reaching an alarming level. PCM have been used in energy storage, transport, textile & buildings applications. For the construction industry, responsible of almost 60% of greenhouse gases worldwide in 2016 [3], PCM can be integrated in walls or ceiling [4]. Thus, reducing temperature fluctuations throughout the day (more time in comfort zone). By delaying the peak of temperature, it also enables to lower blackout eventualities of the electrical network. Such technologies help decreasing the peak of energy demand and cost of electricity during on-peaks [5]. PCM represent a wide range of materials going from inorganics materials such as metallics, to organic ones like paraffinic compounds or natural/biodegradables ones such as fatty acids or sugar alcohols [6]. Eutectics are also studied, helping lowering the range temperature of the final products making it modular according to the intended application. Inorganics provide great amount of energy stored but are corrosive and chemically unstable. Organics coming from petroleum are great in numerous aspects but not sustainable. Thus, this work focused on biodegradable/natural PCM. Besides being obtained by non-polluting reactions, they offer great properties such as a wide range of temperature (-5 to 76°C), non-toxicity and chemical stability [7]. The PCM can be used alone or incorporated in matrices (wood, concrete, geopolymers, ...) *via* different ways such as direct incorporation, immersion (capillarity) or encapsulation (macro or micro) [4]. Immersion method had some issues of leaks and thus, can provoke flammability of the material [8]. The direct method is faster and cheaper than the other ones. Using this method, several organic liquids have already been successfully incorporated into solid matrices, such as geopolymers for building application [9]. However, the direct incorporation of liquid biobased PCM such as fatty acid in the geopolymer matrix can be difficult. Due to a huge increase of viscosity of the fresh geopolymer paste, mixing and homogenization become laborious. Therefore, to avoid direct contact of the bio-based PCM containing acid groups with the alkaline activating solution of the geopolymeric medium, the PCM can be protected by encapsulation with $CaCO_3$. In this respect, due to the great chemical inertia of alkanes, paraffinic PCM will be used as standard, to evaluate the $CaCO_3$ encapsulation process. Such

paraffinic PCM can be directly incorporated in geopolymer matrix [9] and encapsulated [10]. N-eicosane (T_m = 37°C) has been chosen as a PCM standard for tryouts before applying this strategy with biobased PCM, known to be more laborious for incorporation.

Materials & methods:

Materials:

n-eicosane with a purity of 99% used as a PCM & Red Soudan (III) added as red dye for optical analysis were purchased from Sigma-Aldrich, USA. Sodium dodecyl benzene sulfonate (SDBS) was employed as an anionic surfactant and supplied by Aldrich, USA. Calcium chloride ($CaCl_2$) & Sodium carbonate (Na_2CO_3) were the reactants chosen to form the $CaCO_3$ shell and obtained with Carlo Erba.

Preparation of Eicosane@$CaCO_3$ (Mechanical Stirrer) composites:

0,122 g of SDBS has been poured in 10 mL of distilled water and mixed with a cross-shaped stirrer rotating at 750 rpm. The solution was stirred in a double walled beaker and thermoregulated at 50°C thanks to a heated bath. Then 2 g of red dyed (Soudan red (III)) n-eicosane were added for 20 minutes. 30mL of an aqueous solution of $CaCl_2$ at 0.66 M has been added dropwise over 4h with a vigorous agitation (750 rpm). Followed by a dropwise addition over 6h of 30 mL of Na_2CO_3 with the same molar concentration.

The pinky-obtained suspension was centrifuged at 5000 rpm for 5 minutes and washed twice with distilled water. Dried Eicosane@$CaCO_3$ (MS) composites were obtained after 48h at 35°C.

Preparation of Eicosane@$CaCO_3$ (Ultra-Turrax) composites:

The dispersion of colored eicosane in the surfactant is realized using an Ultra-Turrax IKA, T18 digital at 25 000 rpm for one minute. The other steps were carried out as previously exposed. Dried Eicosane@$CaCO_3$ (UT) was thus obtained.

Preparation of Eicosane@$CaCO_3$ (Sonotrode) composites:

For the Eicosane@$CaCO_3$ (S) composite, a sonotrode was used during one minute to form the emulsion.

Characterization:

In this study we used numerous apparatuses to characterize the structural and thermal properties of our samples. For the morphological characterization we used an optical microscope (Digital microscope VHX Keyence with a VH-Z100UR/W/T lens) and a Scanning electron microscope (Hitachi FlexSEM 1000. The secondary electrons were detected with an acceleration voltage of 5kV. The microcapsules were characterized using a spectrophotometer. (Thermo Smart iTR - Nicolet 380 FT-IR) to determine the IR spectrum. To determine the thermal properties of the samples, DSC scans (TA Q2000) were run, as well as TGA (TA Q500), both performed with a 5°C/min heating ramp under nitrogen atmosphere, from 0 to 60°C.
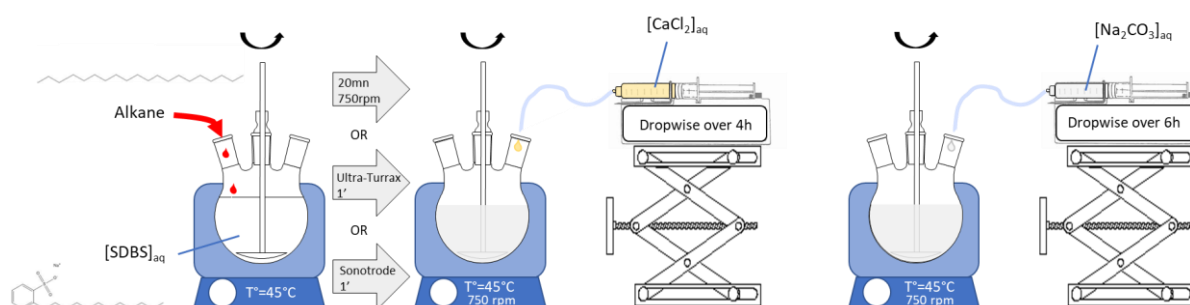
Results & discussion:

Figure 1: Experimental protocol for encapsulation of n-eicosane

The process formation of the microcapsules is obtained *via* self-assembly, relying on attractive forces. The surfactant's role in the aqueous solution is to form an oil-in-water (O/W) emulsion with the oleo-soluble PCM (figure 1). It would form small droplets of emulsions with negatively charged heads outside the PCM's core, making it sensitive to the calcium cations added to the solution. The calcium ions would be linked by electrostatic forces, forming a complex. Then the role of the carbonate anions is to react by precipitation and crystallization on the Ca^{2+} ions attached to the PCM core. Doing so, it will form a layer of precipitated calcium carbonate over the PCM. Hence leading to microcapsules of PCM core inside a $CaCO_3$ shell.

This study focused on improving the thermal properties of the microcapsules, varying the type of agitation before the formation of the calcium complex. These experiments also allow one to evaluate the effect of the droplet size of n-eicosane on the $CaCO_3$ encapsulation's efficiency. Different mixings were used to form the O/W emulsion. First, a mechanical stirrer was used as a representative baseline at 750 rpm for 20 minutes. It was compared to the microcapsule obtained with the emulsion formation with an Ultra-Turrax at 25 000 rpm for 1 minute and with a sonotrode at 12W and 100% amplitude for 1 minute.

Morphology

Figure 2: Optical microscopy of the reactional medium after the last addition of Na_2CO_3. From left to right, Eicosane@$CaCO_3$ (MS), (UT) and (S)

Optical microscopic images were taken to exhibit the core-shell morphology according to the emulsification process chosen at the end of the reaction. Most of the reactional medium present spherical shape with sizes depending on the stirring (Figure 2). Bigger size of microcapsules was obtained with the mechanical stirrer; smaller sizes were obtained with the Ultra-turrax while the smallest capsules were obtained with the help of the sonotrode. These different stirring methods allows to reach microcapsules of smaller sizes with the sonotrode compared to the mechanical stirrer & the ultra-turrax. Independently of the stirring method, there is smaller grains (~ 3µm) in the medium. They have been identified as $CaCO_3$ in the literature. Indeed Ca^{2+} and CO_3^{2-} in aqueous solution tend to form amorphous crystallites [11-12].

Infra-red analysis

The objective of this characterization is to show the presence of similar vibrations peaks proving the presence of the components in the synthesized sample. The FTIR spectra of Eicosane@CaCO3 (MS) is compared to n-eicosane and commercial calcium carbonate (figure 3). The sample obtained with the mechanical stirrer (MS) is considered as a reference for the encapsulation process.
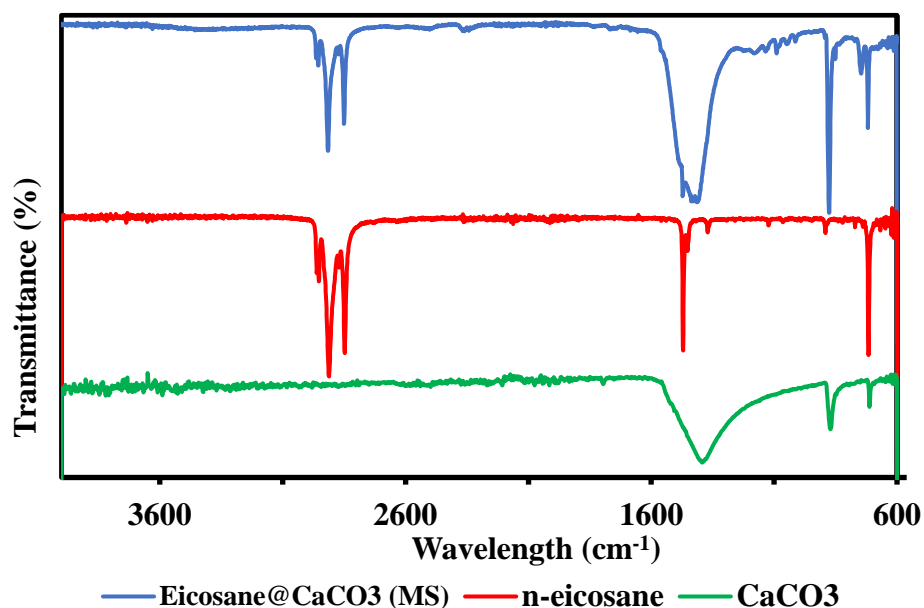
Figure 3: Infra-red spectrum of n-eicosane, $CaCO_3$ and Eicosane@$CaCO_3$ (MS)

The vibration band in the $CaCO_3$ spectrum at 714 cm^{-1} is attributed to C-O bond out-of-plane bending. The peaks at 867 cm^{-1} and broad band at 1450 cm^{-1} correspond to C-O bonds in-plane bending and asymmetric stretching mode, respectively. [13] The n-eicosane spectrum shows characteristics stretching peaks of C-H bonds at 716, 1470, 2840, 2900 and 2950 cm^{-1}. [14]. The vibration prints of n-eicosane and $CaCO_3$ are observed in the spectrum of Eicosane@$CaCO_3$. Indeed, the peaks at 716, 1470, 2840, 2900 and 2950 cm^{-1} corresponding to n-eicosane are found in the Eicosane@$CaCO_3$ spectrum, corresponding to the presence of n-eicosane in our sample. Moreover, the peaks at 867 and the broad band at 1400 cm^{-1} corresponding to $CaCO_3$ is also overlapped in the analysis obtained for the synthesized sample. These results thus confirm that precipitation of calcium carbonate occurred during the process of encapsulation. n-eicosane is still present in the sample, it goes accordingly with the objective of core/shell protection. The different peaks listed of calcium carbonate and n-eicosane previously, can also indicate their proportion in the sample encapsulated n-eicosane once their relative intensities are compared.

DSC and TGA analyses:

Phase change material and microcapsules 's thermal properties were investigated by DSC (Table 1, figure 4) and TGA (table 1, figure 5).
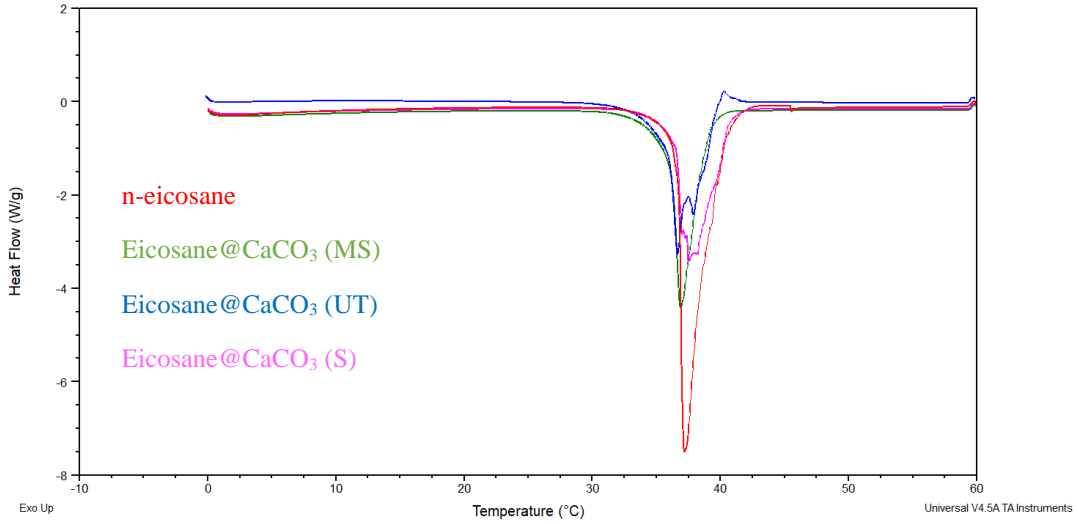
Figure 4: DSC analysis of n-eicosane, Eicosane@CaCO₃ (MS), Eicosane@CaCO₃ (UT) and Eicosane@CaCO₃ (S)

The characteristic melting peak of the PCM (here eicosane) is observed at 37°C on the DSC curve (figure 4) [15]. The melting enthalpy of the pure PCM is 242J/g. However, the enthalpy is reduced to 126 J/g, 116 J/g, 128 J/g for the mechanical stirrer, the ultra-turrax and the sonotrode, respectively. The shape and intensities of n-eicosane and Eicosane@CaCO₃ samples are different in shape and intensities This suggests a different behavior of the n-eicosane in the samples, tending towards confirming the encapsulation. In numerous studies, if not all, the ratio of encapsulation is calculated with the formula following:

$$\frac{melting\ enthalpy\ of\ the\ sample}{melting\ enthalpy\ of\ pure\ PCM} \times 100 \qquad (1)$$

Encapsulation ratio was found to be around 50%, regardless of the emulsification method.

Sample	Melting enthalpy, (J/g)	Encapsulation ratio %R (DSC)	Encapsulation ratio %R (TGA)
n-eicosane	242	/	/
Eicosane@CaCO₃ (MS)	126	52	55
Eicosane@CaCO₃ (UT)	116	48	47
Eicosane@CaCO₃ (S)	128	53	55

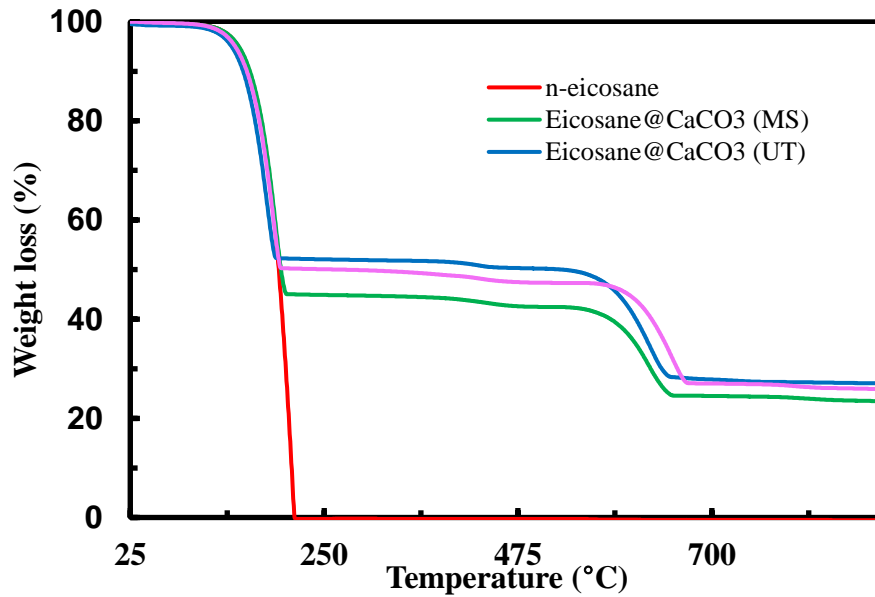Table 1: DSC and TGA results of the Eicosane@CaCO₃ composites

TGA analysis:

Figure 5: TGA analysis of n-eicosane, Eicosane@CaCO$_3$ (MS), (UT) and (S)

The thermal stability is one of the most important parameters of phase change materials. The degradation behavior of the samples encapsulated was compared to the degradation of pure n-eicosane (figure 5). On TGA experiment of pure n-eicosane, a weight loss is detected in a one-step decomposition at 190°C. On the TGA experiments of the microcapsules, two weight losses are observed. The first one at 190°C is similar to the thermal decomposition of pure n-eicosane and can be related to a leak of encapsulated n-eicosane under gas form through the CaCO$_3$ shell [13]. The loss percentages are around 50% (for all the stirring methods) and confirm the results of encapsulation ratio performed by the DSC apparatus. The 2nd weight loss can be attributed to the degradation of the CaCO$_3$ shells into CaO and CO$_2$. Since reaction (1) and using the molar masses of these elements, it allows one to attribute this weight loss to CO$_2$. Indeed, the CO$_2$ degradation would represent 56% of the CaCO$_3$ compound, resulting in 44% of CaO residues in the apparatus afterward.

$$CaCO_3 \rightarrow CaO + CO_2 \ (2)$$

Conclusion:

One of the main objectives of this paper was to compare the effect of emulsification process of the n-eicosane in an aqueous solution of SDBS as surfactant on the properties of the microcapsules. With the three methods of stirring, it is possible to encapsulate n-eicosane inside a calcium carbonate shell, with a greater than 50% encapsulation ratio. Thermal characterization

has been performed with DSC and TGA, which are complementary tests. The first one gives information about the melting enthalpy and obtain information on the encapsulation ratio. The second analysis allows to obtain numerous data such as thermal degradation and shell composition. Thermal degradation also provides information about the encapsulation ratio and thus, can be compared with the ratio obtained by DSC. It has been proved that microcapsules with n-eicosane core and calcium carbonate shell was produced. The feasibility of encapsulation is proven; the next stage will be to incorporate pure n-eicosane as well as Eicosane@CaCO$_3$ in a cementitious matrix.

References / Bibliography

[1] Milián, Y. E., Gutiérrez, A., Grágeda, M., & Ushak, S. (2017). A review on encapsulation techniques for inorganic phase change materials and the influence on their thermophysical properties. Renewable and Sustainable Energy Reviews, 73, 983–999

[2] Srinivasaraonaik, Singh, L. P., Tyagi, I., Rawat, A., & Sinha, S. (2020). Microencapsulation of a eutectic PCM using in situ polymerization technique for thermal energy storage. International Journal of Energy Research, 44(5), 3854–3864

[3] Martinez, S., Delgado, M. del M., Martinez Marin, R., & Alvarez, S. (2019). Identifying the environmental footprint by source of supply chains for effective policy making: the case of Spanish households' consumption. Environmental Science and Pollution Research International, 26(32), 33451–33465

[4] Al-Absi, Z. A., Mohd Isa, M. H., & Ismail, M. (2020). Phase change materials (PCMs) and their optimum position in building walls. Sustainability, 12(4), 1294

[5] Junaid, M. F., Rehman, Z. ur, Ijaz, N., Čekon, M., Čurpek, J., & Babeker Elhag, A. (2022). Biobased phase change materials from a perspective of recycling, resources conservation and green buildings. Energy and Buildings, 270(112280), 112280

[6] Zhang, H., Xu, C., & Fang, G. (2022). Encapsulation of inorganic phase change thermal storage materials and its effect on thermophysical properties: A review. Solar Energy Materials and Solar Cells: An International Journal Devoted to Photovoltaic, Photothermal, and Photochemical Solar Energy Conversion, 241(111747), 111747

[7] Farid, M. M., Khudhair, A. M., Razack, S. A. K., & Al-Hallaj, S. (2004). A review on phase change energy storage: materials and applications. Energy Conversion and Management, 45(9–10), 1597–1615

[8] Fang, X., Zhang, Z., & Chen, Z. (2008). Study on preparation of montmorillonite-based composite phase change materials and their applications in thermal storage building materials. Energy Conversion and Management, 49(4), 718–723

[9] Barneoud-Chapelier, A., Causse, J., & Poulesquen, A. (2020). Synthesis of geopolymer emulsions. Materials Letters, 276(128188), 128188

[10] Jiang, Z., Yang, W., He, F., Xie, C., Fan, J., Wu, J., & Zhang, K. (2018). Microencapsulated paraffin phase-change material with calcium carbonate shell for thermal energy storage and solar-thermal conversion. Langmuir: The ACS Journal of Surfaces and Colloids, 34(47), 14254–14264

[11] Zhang, J.-L., Wu, X.-W., Ke, W.-D., & Li, Z.-B. (2020). A well encapsulating stearic acid composite phase change material sealed by calcium carbonate. Phase Transitions, 93(1), 100–115

[12] Sarı, A., Saleh, T. A., Hekimoğlu, G., Tyagi, V. V., & Sharma, R. K. (2021). Microencapsulated heptadecane with calcium carbonate as thermal conductivity-enhanced phase change material for thermal energy storage. Journal of Molecular Liquids, 328(115508), 115508

[13] Liu, M., Kang, M., Chen, K., Mou, Y., & Sun, R. (2018). Synthesis and luminescent properties of CaCO3:Eu3+@SiO2 phosphors with core–shell structure. Applied Physics. A, Materials Science & Processing, 124(3)

[14] Maithya, O. M., Li, X., Feng, X., Sui, X., & Wang, B. (2020). Microencapsulated phase change material via Pickering emulsion stabilized by graphene oxide for photothermal conversion. Journal of Materials Science, 55(18), 7731–7742

[15] Alkan, C., Sarı, A., & Karaipekli, A. (2011). Preparation, thermal properties and thermal reliability of microencapsulated n-eicosane as novel phase change material for thermal energy storage. Energy Conversion and Management, 52(1), 687–692