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# Facile approach to improve solar thermal energy storage efficiency using encapsulated sugar alcohol based phase change material

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ABSTRACT

Development of novel solar-based energy storage technologies are considered to be one of the primary solutions to fulfill the energy demand. Sugar alcohol based phase change materials are gaining more attention as a storage medium in thermal energy storage applications. The current study focuses on the synthesis of D-Mannitol (DM) based capsules using the sol-gel technique. The main objective is to control the seepage of DM during phase transition and to increase the thermophysical properties of DM. The synthesis is carried out with pH ranging from 2.0 to 7.0. SEM images showed a well-defined morphology with the uniform spherical shape at pH between 2.6 and 3.0. FTIR spectrum showed the characteristic peaks of silica and DM which suggested the successful encapsulation of DM with silica shell from TEOS source. The average particle size of the microencapsulated DM (MEDM) varied in the range of 45–60 μm. MEDM is subjected to thermal cycling to study the change in heat transfer properties upon cycling. The thermal conductivity of MEDM is found to be 1.77 W/m K, an increase from 1.32 W/m K of DM. From DSC thermograms, the encapsulation ratio and efficiency were observed to be 89.60% and 85.02% respectively. DM exhibited a subcooling temperature of 44.21 °C which was reduced to 11 °C for MEDM. DM is found to degrade initially at a temperature of 276 °C whereas MEDM is found to be 302 °C. The charging and discharging characteristics showed that the time taken to complete one cycle by MEDM lowered compared to DM. The characteristic study of MEDM reveals that it can be used as potential PCM in solar thermal energy storage system.

## 1. Introduction

Thermal energy storage (TES) has been identified as a promising approach for realizing a sustained use of energy for heating and cooling, solar energy harvesting, and other energy-related applications. It plays a crucial role in keeping up with the rising energy demand. Latent heat energy storage is most promising and attractive due to its compactness and ability to store energy at a nearly constant temperature corresponding to the phase transition temperature of the material [1,2]. Phase change materials (PCM) produce a significant amount of thermal energy (latent heat or heat of fusion) through their phase transformation from liquid to solid. They are usually used as the heat storage medium in latent heat energy storage systems. Different types of PCM such as organic, inorganic, and eutectics exist in a wide range of melting/freezing points. The low thermal conductivity of PCM influences the charging (energy absorption; melting) and discharging (energy release; solidification) process, which leads to reduced efficiency of the energy storage system [3]. Sugar alcohols such as Threitol, Allitol, Iditol, Erythritol, Mannitol, Dulcitol and their eutectic mixtures have advantages of a broad range of melting temperatures, high volumetric energy densities, non-corrosive nature, and high thermal stabilities which makes them promising candidates for use in TES applications [4]. Vacuum impregnation method was used by [5] to control the melting point of DM in nanosized porous $SiO_2$ grains. They found that the melting point dropped to 140 °C due to the presence of nonfreezing liquid layer at the interface. The thermal degradation of DM in $SiO_2$ composite was found to be ten times more than pure DM. Reduced graphene oxide was used as an additive to boost the thermal conductivity of n-eicosane by [6] and found the reduced graphene oxide from sodium borohydride increased the conductivity by 83% with 6% reduction in phase change enthalpy. Conductivity was found to increase by 193% with 15% loss in phase change enthalpy for thermal reduced graphene oxide. Lauric acid was dispersed in $SiO_2$ as a composite PCM by [7] and prevented the melting of Lauric acid even above its melting

*Abbreviations:* DM, D-Mannitol; MEDM, Microencapsulated D-Mannitol; SEM, Scanning electron microscope; FT-IR, Fourier transform infrared spectroscopy; TEOS, Tetraethylorthosilicate; DSC, Differential scanning calorimetry; TES, Thermal energy storage; PCM, Phase change material; PMMA, Polymethylmethacrylate; MTEOS, Triethoxymethylsilane; SDS, Sodium dodecyl sulphate; DTA, Differential thermal analysis; TGA, Thermogravimetric analysis; LFA, Laser flash apparatus; pH, Hydrogen potential

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**Symbols**

| | |
|---|---|
| $k$ | Thermal conductivity |
| $\alpha$ | Thermal diffusivity |
| ρ | Density |
| $c_p$ | Specific heat capacity |
| $E$ | Encapsulation efficiency |
| $R$ | Encapsulation ratio |

*Units*

| | |
|---|---|
| μm | Micrometer |
| W/m K | Unit of thermal conductivity |
| °C | Degree Celsius |
| kJ/kg | Unit of specific enthalpy |
| kJ | Unit of enthalpy |
| rpm | Revolutions per minute |
| g | Grams |
| mm | Millimeter |
| V | Volt |
| $mm^2/s$ | Unit of thermal diffusivity |
| ml/min | Milliliter per minute |
| $cm^{-1}$ | Wavenumber in FTIR spectrum |
| °C/min | Heating and cooling rates |
| bar | Unit of pressure |
| $kg/m^3$ | Unit of density |

point. The composite was found to melt at 42.46 °C with an enthalpy of 117.21 kJ/kg and solidifies at 41.30 °C with an enthalpy of 90 kJ/kg. Silver coated nanocapsules of octadecane were prepared by [8] using dopamine surface activation followed by electroless plating on silica nanocapsules. They found that the silver coating resulted in a decrease of mass-based latent heat with a minor decrease of volume based latent heat. The conductivity increased from 0.25 to 1.35 W/m K. The influence of oxidation degrees of graphene oxide on thermal properties of MEPCM was studied by [9] and found that graphene oxide had an influence on thermal conductivity and hardly affected the morphology and latent heat of the capsules.

Encapsulation is a process in which the phase change material is isolated in an inert shell which tends to hold the PCM, and the solid-liquid transition takes place inside the shell. This is done to prevent the PCM from reacting with the external environment and to increase the heat transfer properties of PCM [10]. The methods to encapsulate a PCM can be broadly classified into three types- physical, chemical and physio-chemical methods. In the physical method, the ingredients do not undergo any chemical reaction, and the encapsulation layer is formed by pan coating or suspension coating or spray drying. The main disadvantage is the complex morphology of the formed capsules. Chemical methods are the one in which polymerization reaction is initiated when the free radicals attack the monomers when there is a change in pH. These chemical methods can be further classified into suspension, emulsion, interfacial, in-situ and condensation polymerization. The suspension method is preferred when either the monomers or initiators are poorly soluble in the aqueous phase (usually water). The emulsion method is used to synthesize organic shells of PMMA (Polymethylmethacrylate) and polystyrene. The interfacial method is preferred when the monomer or initiator is hydrophobic, and the other is hydrophilic. In the in-situ technique, instead of monomers, chemicals which produce the precursor to the polymer shell are used. Melamine-Formaldehyde based organic shells are synthesized in this process, but the toxicity and environmental effects of formaldehyde are of concern. The condensation method is a part of the in-situ method, where the reaction releases water and methanol as by-products from alcohol, amino or carboxyl groups [11]. The physio-chemical method is a combination of both physical and chemical methods which include phase separation, heating and cooling along with hydrolysis and condensation reactions. They can be further classified into the sol-gel technique and complex coacervation. Complex coacervation method is typically used for organic shell materials like gelatin/gum-arabic, agar-agar/gum-arabic, chitosan/gum-arabic, chitosan/silk-fibroin, etc whereas the sol-gel technique is used to synthesize inorganic capsules such as silica or titanium oxide. Organic polymers are usually toxic and flammable when compared to inorganic polymers and also have poor thermal properties. Due to these disadvantages, inorganic materials such as silica, silicon dioxide, and titanium dioxides are used as the shell material [11].

Sol-gel technique has been focused in the current study owing to enhanced thermal properties of the shell material compared to other techniques of encapsulation. Encapsulation of phase change materials through sol-gel technique can be represented as the formation of an inert silica shell through a polycondensation reaction of the silica monomer source in a liquid. When the prepared sol solution is added to the PCM emulsion, microcapsules of PCM in a shell were formed. The sol solution is prepared through hydrolysis of silica precursors such as TEOS (Tetraethylorthosilicate) or sodium silicate or MTEOS (Triethoxymethylsilane), etc. pH between 2 and 3 is to be maintained to promote the hydrolysis of the precursor chemical. Then the silicate sol solution will be added dropwise to the PCM oil-water emulsion with continuous stirring to allow the formation of silica shell around PCM. In sol-gel encapsulation, silica particles surround the flavor molecules during gel formation. In principle, the sol-gel process can be considered as a phase separation through sol-reactions, sol–gelation and finally, the removal of the solvent resulting in a ceramic material [12].

Many researchers have explored on encapsulating PCM using the sol-gel technique. Zhang et al. [13] encapsulated Octadecane in a silica shell using interfacial polycondensation with TEOS (Tetraethylorthosilicate) as silica precursor. They found particle size to be 17 μm when the pH is maintained at 2.89, and the capsules had a significant increase in thermal conductivity owing to the high thermal conductivity of the silica shell. The enthalpy was found to be as 214.6 kJ/kg and 216.2 kJ/kg for melting and solidification respectively. Triethoxymethylsilane was also used as a precursor to encapsulate Octadecane [14]. The enthalpies were found to be 227.66 kJ/kg and 226.26 kJ/kg for melting and solidification respectively. The regular spherical shape of n-eicosane with an outer silver layer was synthesized by [15] using interfacial polycondensation, and the phase change enthalpies were found to decrease with pure n-eicosane. Sodium silicate was used as silica precursor to encapsulate octadecane by [16], and a spherical shell was synthesized with pH between 2.92 and 3.05. They concluded that the phase change enthalpies of the capsules mainly depended on the core loading in the capsules. Fire resistant $SiO_2$ shell material was used to encapsulate paraffin by [17] using the sol-gel technique. The paraffin capsules were found to have a melting latent heat of 165.68 kJ/kg with the melting point as 58.37 °C and encapsulation efficiency of 87.5%. Sol-gel technique was used to encapsulate n-eicosane with a titanium dioxide shell using tetrabutyl titanate as titania precursor by [18]. The particle size varied from 1.5 to 2.0 μm and had a smooth and compact shell. n-eicosane based microcapsules with titanium oxide shell, modified with graphene nanosheets were synthesized by [19] using interfacial polycondensation technique. They found that the encapsulation rate and microstructure formation was low when the water content in the aqueous phase was high. Therefore, formamide was used as the solvent instead of water to make the reaction aqueous free, which resulted in uniform sized capsules. Graphene sheets adhered to the shell material increasing the thermal