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# Thermophysical properties of *n*-tetradecane@polystyrene-silica composite nanoencapsulated phase change material slurry for cold energy storage

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ABSTRACT

Based on the synthesis of *n*-tetradecane@polystyrene-silica (Tet@PS-$SiO_2$) composite nanoencapsulated phase change material (NEPCM), a novel composite NEPCM slurry for cold energy storage was prepared by dispersing NEPCM into base fluid. The thermal performances of the Tet@PS-$SiO_2$ NEPCM were measured by differential scanning calorimetry (DSC) and thermogravimetric analyzer (TG). The thermophysical properties of the NEPCM slurry including morphology, particle size, specific heat capacity, thermal conductivity, viscosity and mechanical stability were investigated systematically. The results showed that the Tet@PS-$SiO_2$ NEPCM had a melting latent heat of 83.38 kJ $kg^{-1}$ and excellent thermal stability. Transmission electron microscope (TEM) images displayed that the synthesized nanocapsules had regular spherical core-shell structure, and particle size analysis of NEPCM dispersed in slurry showed the mean particle size of Tet@PS-$SiO_2$ NEPCM was 151.3 nm. Moreover, the Tet@PS-$SiO_2$ slurry had a high specific heat capacity and obtained an enhancement 8.4% in thermal conductivity by the grafting of $SiO_2$ on the PS shell. In addition, the slurry showed an acceptable viscosity and excellent mechanical stability. Those results indicate the Tet@PS-$SiO_2$ slurry can be considered as an up-and coming latent heat fluid for cold energy storage.



## 1. Introduction

In recent years, cold energy storage technology has been widely used in air-conditioning systems as it can balance the mismatch between the supply and demand of electricity. It is known that efficiency is limited for traditional cold energy storage technology since the cold energy storage and transmission processes are completed by two separate media. Therefore, the latent functionally thermal fluid (LFTF) prepared by adding a certain amount of phase change material (PCM) to base fluid has been proposed. Apart from being as a cold energy storage medium, LFTF can serve as a transfer heat medium for pipeline as part of storage tank. The same medium is used for both cold energy storage and transmission improving the efficiency for air-conditioning systems.

In general, the LFTF is divided into two categories including phase change material emulsion (PCE) and microencapsulated PCM slurry (MEPCMS). Several researches [1–5] observed that cold energy storage capacity of PCE showed a fascinating enhancement since PCM releases latent heat during phase transition process. Delgado et al. [6] confirmed that thermal storage capacity of PCE containing paraffin increased by 50% compared to water. However, PCE with a certain amount of emulsifier is likely to block pipeline due to its high viscosity and relatively large flow resistance, especially during the solid-liquid phase transition. Hence, more and more researchers have turned their attentions to MEPCMS which is prepared by dispersing microencapsulated PCM into base fluid. Owing to large surface area, acceptable viscosity as well as micro-convection effects between microcapsules and base fluid, the MEPCMS exhibits excellent heat transfer performance. Chen et al. [7] found out that heat transfer performance of 15.8 wt.% MEPCMS in a circular tube was 1.42 times more than that of water under laminar flow condition. Based on reviewing experimental and theoretical investigations on energy performance in PV/T system using MEPCMS consisting of microencapsulated paraffin by polymer shells as working fluid by Qiu et al. [8,9], the net overall solar efficiency of this system could reach 80.8-83.9% at recommended

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**Nomenclature**

| | |
|---|---|
| PCM | Phase change material [-] |
| PCE | Phase change material emulsion [-] |
| MEPCMS | Microencapsulated PCM slurry [-] |
| Tet | N-tetradecane [-] |
| PS | Polystyrene [-] |
| NEPCM | Nanoencapsulated phase change material [-] |
| LFTF | Latent functionally thermal fluid [-] |
| $C_p$ | Specific heat capacity [J g$^{-1}\cdot{}^{\circ}$C$^{-1}$] |
| $T_{initial,m}$ | Initial melting temperature [°C] |
| $T_{initial,c}$ | Initial crystal temperature [°C] |
| $\Delta H_m$ | Melting latent heat [kJ kg$^{-1}$] |
| $\Delta H_c$ | Crystal latent heat [kJ kg$^{-1}$] |

*Subscripts*

| | |
|---|---|
| initial | Onset melting or crystal |
| m | Melting process |
| c | Crystal process |

operational conditions. Delgado et al. [10] observed that the mass fraction of microencapsulated paraffin had significant impact on thermal and rheological characterizations of MEPCMS and the 20 wt.% slurry had optimum heat transfer performance when flowing through a circular tube. Experiments conducted by Wang et al. [11] stated that heat transfer performance of microencapsulated paraffin slurry in parallel microchannels could be enhanced as 1.34 times of that of pure water. Wang [12] and Ma [13] et al. accomplished studies on heat transfer characteristics of MEPCMS in the circular tube by experiment and simulation, respectively. Besides that, researches on heat transfer performances of MEPCMS in rectangular heat storage tank [14], coil heat exchanger [15] and vertical pipe [16] were also investigated. These research results showed heat transfer performances of these slurries increased in comparison with water as a result of the addition of microencapsulated PCM particles.

Nonetheless, the microcapsules in large size particles could easily fracture when were used for slurry during long term circulating [17]. Therefore, further investigations on nanoencapsulated phase change material (NEPCM) slurry have been performed. Seyf et al. [18,19] conducted numerical simulations of NEPCM (nanoencapsulated *n*-octadecan) slurry in a unconfined square cylinder and microtube heat sinks with tangential impingement. They found that the use of NEPCM slurry could enhance heat transfer characteristics, while caused higher shear stress compared to base fluid. Rajabifar and his coworkers [20] using a three dimensional numerical model investigated the effects of nanocapsules volume fraction, inlet velocity and wall temperature on the thermal and hydrodynamic performances in micro pin fin heat sink. The results showed that the significant heat transfer enhancement was achieved when using NEPCM slurry as an advanced coolant. Barlak et al. [21] showed thermal conductivity of NEPCM (nanoencapsulated *n*-nonadecane by polyurethane) slurry were 1.2 times more greater than that of water for slurry of 3.36% volume fraction of nanocapsules. The study on heat transfer performance of polymer/paraffin NEPCM slurry was carried out by Wu et al. [22]. The experimental results showed that compared to base liquid, the heat transfer coefficients of slurry with 28% volume fraction of nanocapsules risen by 50% and 70% for jet impingement and spray cooling, respectively.

It is understandable that NEPCM as dispersed phase plays a crucial rule on both thermophysical and heat transfer performances of slurry. Whether for experimental or numerical simulation studies, the shells of NEPCMs used for slurries were all polymeric materials so far. As everyone knows, these shells have the drawback of lower thermal conductivity, which will decrease thermal conductivity of slurry when NEPCMs were dispersed in slurry. Therefore, our team proposed that NEPCMs with organic/inorganic composite shell were used as a dispersed phase to improve thermal conductivity of slurry. Usually, the thermal conductivity of inorganic materials is higher than that of the polymeric ones. Hence, the thermal conductivity of slurry may be enhanced by grafting inorganic material on the polymer shell of NEPCMs when NEPCMs were dispersed in slurry. Among numerous inorganic materials, the $SiO_2$ was most frequently studied as the shell of microcapsules and nanocapsules because of its good thermal conductivity as well as mechanical strength. Therefore, our team designed an experiment that NEPCM with organic/$SiO_2$ composite shell was dispersed in base fluid to form composite NEPCM slurry. To the best of our knowledge, the investigation on composite NEPCM slurry has not been reported in published literatures.

In this paper, using *n*-tetradecane (Tet) with the suitable phase change temperature (5.8 °C) in operating temperature range of air-conditioning systems (5–12 °C) as core, and polystyrene (PS) and silica ($SiO_2$) as composite shell, a novel Tet@PS-$SiO_2$ NEPCM slurry for cold energy storage was obtained by dispersing NEPCM into base fluid. The thermophysical properties of the Tet@PS-$SiO_2$ slurry such as morphology, particle size, specific heat capacity, thermal conductivity, viscosity and mechanical stability were mainly discussed, which provides a complete basis for further practical application in cold energy storage.

## 2. Materials and methods

### 2.1. Materials

Styrene (St), ethylene glycol dimethacrylate (EDMA) and methyl methacrylate (MMA) (AR, from Tianjin Damao Chemical Regent Plant, China) were sequentially washed for three times with aqueous solution of 10 wt.% sodium hydroxide and deionized water, respectively, then reserved in the refrigerator storage before used. *n*-tetradecane (Tet), 2,2-azobis (2,4-dimethyl) valeronitrile (AIVN), sodium dodecyl sulfate (SDS), poly-(ethylene glycol) monooctylphenyl ether (OP-10), silane coupling agent KH-570, tetraethoxysilane (TEOS), ammonium hydroxide ($NH_3\cdot H_2O$) and ethylene glycol (EG) were used directly without further purification.

### 2.2. Preparation of NEPCM

According to the literature [23], the similar synthesis procedure of *n*-tetradecane@polystyrene-silica NEPCM(recorded as Tet@PS-$SiO_2$)was conducted. Fig. 1 shows synthesis schematic of Tet@PS-$SiO_2$ NEPCM. The polymerization reaction required to pass through following steps: (1) formation of small droplets containing compatible Tet and St droplets; (2) in situ miniemulsion polymerization of small droplets; (3) generation of hydrophilic silica nanoparticles by sol-gel reaction of tetraethoxysilane (TEOS); (4) hydrophobic modification of silica nanoparticles using KH-570 coupling agent; (5) formation of Tet@PS-$SiO_2$ NEPCM.

The typical synthesis procedure was as follows: modified silica sol was first self-made by hydrolysis-condensation of TEOS and modification of KH-570 using $NH_3\cdot H_2O$ at 60 °C for 3 h. An oil phase mixture was obtained by mixing 10 g St, 0.8 g MMA, 0.08 g AVBN, 10 g Tet and 0.1 g EDMA together, and aqueous solution was obtained by mixing 0.3 g SDS, 0.3 g OP-10 and 100 g deionized water together. After adding aqueous solution into oil phase, the resultant mixture was emulsified by homogenizer (model FJ200-S, Shanghai Specimen and Model Factory, China) at 6000 rpm for