



# Supercooling suppression and thermal behavior improvement of erythritol as phase change material for thermal energy storage



Yi Wang<sup>a,b,\*</sup>, Shuang Li<sup>b</sup>, Ting Zhang<sup>b</sup>, Deyi Zhang<sup>a</sup>, Hui Ji<sup>b</sup>

<sup>a</sup> State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals, Lanzhou University of Technology, Lanzhou 730050, PR China

<sup>b</sup> College of Petrochemical Technology, Lanzhou University of Technology, Lanzhou 730050, PR China

## ARTICLE INFO

### Keywords:

Phase change material  
Supercooling suppression  
Erythritol  
Thermal-physical property  
Thermal energy storage

## ABSTRACT

The main aim of this paper is to mitigate the supercooling and improve the heat release performance of erythritol (ET) as phase change material for thermal energy storage using the method of encapsulation and doping additives. The capsules containing ET, thickening and nucleating agent were prepared and various characterization techniques were employed to investigate the structure and thermo-physical properties of the composite, especially the supercooling inhibition and exothermicity improvement. Experimental results reveal that capsulation and adding thickening and nucleating agents have positive influence on the supercooling elimination, heat discharging ability improvement and thermal stability enhancement. The optimal capsules, with the maximal ET mass percentage of 59.2%, melt at 121.2 °C and freeze at 106.4 °C with the latent heat of 213.3 J/g and 206.9 J/g, respectively. Due to the improved crystallization kinetics, the degree of supercooling decreased by 83.6% as well as the heat release ratio increased by 52.2% compared to those of pristine ET. The as-prepared capsules have obvious core-shell structure, good compatibility between the shell and core materials. The thermal conductivity is 0.84 W/m K, increased by 29.2% than that of pristine ET. The results of accelerated thermal cycling test indicate that the supercooling, heat release ability and thermal reliability of encapsulated ET changed imperceptibly. In total, the technology of capsulation and adding thickening and nucleating agents can be used to suppress the supercooling and improve the thermal behavior of ET.

## 1. Introduction

Latent heat thermal energy storage (LHTES) is one of the most competent ways, and now emerging with considerable momentum for developing renewable energy and improving the efficiency of energy utilization [1]. The thermal energy storage medium in LHTES is called phase change material (PCM) which is characterized by storing or releasing large amount of latent heat while changing from one phase to another within a small range or at a specific temperature [1,2]. Until now, more than 160,000 [3] chemical substances including salt hydrates, polyols, paraffins, fatty acids, fatty acid esters and their mixtures were investigated as PCM to meet a variety of freezing/melting points [4]. From the literature review, the PCMs with the phase change temperature between 0 and 60 °C aiming to low temperature application, e.g. building energy conservation, domestic heating/cooling and biomedical products, received more attention [5,6], while the PCMs with melting point about 100 °C were seldom to survey relatively. In fact, this emerging PCM category is more suitable for recovering industrial high-temperature waste heat, producing domestic hot water and

manufacturing cold water through an absorption chiller [7]. According to a reliable PCMs' database, erythritol (ET) appears to be a more suitable candidate than other less expensive organics like paraffin and fatty acids owing to its moderate phase change temperature [8]. Erythritol [(CH<sub>2</sub>OH)(CHOH)<sub>2</sub>(CH<sub>2</sub>OH), CAS No.149-32-6], a meso-compound of 1,2,3,4-butanetetrol prepared industrially by glucose fermentation using inexpensive raw as carbon sources [9], exhibits excellent thermo-chemical properties such as good thermal stability, high mass-specific enthalpy (about 340 J/g [9,10] – 379 J/g [11,12]), considerable specific heat (1.68 J/g K<sup>-1</sup> [13]) and moderate phase change temperature (approx. 118 °C) [12,14]. Besides these, the four-carbon sugar alcohol also has the features of renewable origin being plants-based which determines the attributes of safety (even for daily uptake as a common sweetener) [9], environment friendly [15], cost-effectiveness and high compatibility with container [16]. Even so, the knowledge on the thermo-physical properties and phase change behaviors of ET as a desirable PCM for thermal energy storage design is presently sparse and rather inconsistent [8].

The main reason of the scarce information about the four-carbon

\* Correspondence to: State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Lanzhou University of Technology, No. 287, Langongping Road, Lanzhou, Gansu 730050, PR China.

E-mail addresses: [wangyi@lut.cn](mailto:wangyi@lut.cn), [haoyunwangyi1977@163.com](mailto:haoyunwangyi1977@163.com) (Y. Wang).

<http://dx.doi.org/10.1016/j.solmat.2017.06.027>

Received 21 January 2017; Received in revised form 5 June 2017; Accepted 18 June 2017

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sugar alcohol using as PCM may attribute to its inherent drawback of serious mismatch between heat storage and release performance and severe supercooling more than 100 °C [16]. Although almost all of literatures reported that ET possesses a high fusion heat which is much higher than most of molten salts and waxes, the freezing enthalpy of ET is depressed and often is selectively forgotten. As far as we know, only A. Sari [11,12] clearly indicated that ET melt at 118.4 °C with the latent heat of 379.57 J/g and freeze at 36.22 °C with the enthalpy of 255.95 J/g. This solidification enthalpy is about 32.6% less than fusion enthalpy means that only about 67.4% of stored thermal energy can be used. Obviously, this mismatch makes thermal energy storage deviated from the original pathway and it is not acceptable in practical application because ET will not discharge the stored thermal energy in the subsequent use. Therefore, it seems worthwhile to further evaluate the suitability of ET as a PCM and detailedly understand the thermal energy storage performance. The second flaw of ET is its serious supercooling (super cooling, also called subcooling [17]) which is a state where liquid PCMs do not solidify immediately at the normal melting (or freezing) temperature, but start crystallization only after a temperature well below the melting temperature is reached [17–20]. Due to the effects of supercooling, it is difficult to control the heat recovery at a constant temperature, which in turn leads to the quality and application fields reduce of the released heat.

Poor nucleation characteristic and slow crystal growth rate are widely considered to be the possible causes of supercooling for ET [21,22] although the mechanism of supercooling is still not clearly understood [21]. Different attempts were conducted to prevent supercooling or reduce it to a minimum level such as adding nucleating agent or nanoparticle additives [19,20], controlling of the size of the PCM [14,23,24], employing mechanical energy including mechanical vibration, stirring and ultrasonic irradiation [21,22]. I. Kholmanov [19] demonstrated that the continuous ultrathin graphite foams (UGFs) could strongly reduce the subcooling degree of erythritol,  $79 \pm 4$  K to  $67 \pm 4$  K, due to the heterogeneous nucleation of erythritol at interfaces with the graphitic structures. M. Karthik [25] declared that the subcooling behavior of ET in ET/graphite foam composite was reduced up to 55 °C. Y. Liu [20,26] investigated the effects of graphene oxide nanosheets and ultrasonic oscillation on the supercooling degree and nucleation behavior of nanofluids PCMs experimentally and analytically, and the results showed that the supercooling degree and nucleation time reduced by 69.1% and 90.7%, respectively. E.P. Ona [21,22] revealed that ultrasonic irradiation is beneficial for the supercooling relaxation and solidification enhancement of erythritol because ultrasonic irradiation enabled constant fragmentation and effective dispersion of crystals. T. Adachi [23] revealed that the supercooling duration of ET in a glass tube increased with the decrease of supercooling degree and specimen size. L. L. Wei [27] measured the supercooling degree for ET masses from 10 mg to 20 g and revealed that the supercooling degree monotonic increased with the decrease of specimen mass [23].

Recently, micro- or nano- encapsulation technology was also employed to reduce supercooling degree of PCMs. A. Sari [28] and G. Fang [29] indicated that microencapsulation could slightly decrease the supercooling degree of the PCMs. At the same time, Y. Wang [30], X. Tang [31] and S. N. Gunasekara [8] declared that the supercooling is effectively suppressed when it is nanoencapsulated. However, some of researches also reported the opposite discoveries, which claim that there is significant decrease of crystallization temperature and obvious increase of supercooling degree during the freezing process with the dropping of microcapsules diameter [18,32–34]. As an example, M. You [32] described that the crystallization temperature of styrene-divinylbenzene *co*-polymer containing *n*-octadecane (C18) microcapsules was about 10 °C lower than that of pristine PCM. On the other hand, voluminous evidence suggests that dispersing nucleating agent or adding thickening agent prior to encapsulate, such as employing aliphatic alcohol as nucleating agent for short-chain *n*-alkanes [34–36], will

resulted in the reduction of supercooling degree and short of solidification or melting time. However, influences of nucleating agent and thicker on the enthalpy of microencapsulated PCMs (MEPCMs) have not been studied, especially for capsules containing ET.

Preparing microcapsules containing ET for high temperature application, the cornerstone of further investigation about the influence of encapsulation and additive on the crystallization behavior and heat storage/release ability, is still a challenge at present due to the technical difficulties [5,14]. Firstly, as a kind of water-soluble PCM, ET is much more difficult to prepare MEPCMs than oil-soluble PCMs [1,37] since most of fabricating method using water as solvent. Thus, there are rarely studies on MCPCMs with water-soluble PCM. Secondly, ET has an annoying operating temperature (higher than 120 °C). The high phase transition temperature does not only lead to manufacturing difficulty, but also increase the risk of crack in the subsequent usage which generated by the different volumetric thermal expansion coefficient of PCM and shell [5,14,38]. Therefore, preparing ET based capsules and further understanding the relationship between the encapsulation, impurities kinds and amounts on the thermal behavior of ET are necessary and challenging works.

In light of the above discussion, the overall objective of this work is to develop a feasible fabrication technique for the form-stable ET MEPCMs, improve the thermal behavior of ET as a potential PCM for low grade thermal energy storage and further understand the effect of encapsulation, impurity addition on the supercooling suppression. Toward these ends, the encapsulation of embedding erythritol into polysiloxane (pSiO) network for the preparation of ET/pSiO composite MEPCMs through ultraviolet assisted hydrolysis method has been studied, and the effects of encapsulation conditions, amounts of nucleating and thickening agent on the crystallization behavior, especially on the thermal release properties and subcooling degree of ET were investigated. Also, the morphology, structure, thermal reliability and stability, thermal conductivity, heat storage properties of the composite which prepared in the optimum technical conditions, together with those of ET and/or pSiO for comparison purpose, were determined by Fourier transformation infrared spectroscopy (FT-IR), scanning and transmission electron microscope (SEM and TEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and accelerated thermal cycling test (ATC).

## 2. Experimental

### 2.1. Materials

Erythritol (ET, commercial grade), used as phase change material without further purification, was purchased from Tianjin Baishi chemical industry Co. Ltd., China. 3-Methacryloxypropyltrimethoxysilane (MEMO, CAS No.2530-85-0) was sourced from Aladdin, Shanghai biological technology Co. Ltd. and employed as precursor of shell material. Carboxymethylcellulose (CMC) and nano-alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) were selected as thickening and nucleating agent, which supplied by Dadi chemical Co. Ltd., Hangzhou China and Shanghai Zhongli Chemical Co., Ltd, respectively. The other chemicals, ethanol, benzene, toluene and sorbitan monooleate (Span-80), were all designated to be of analytical grade and received from Shanghai Chemical Reagent Co. Ltd. Deionized water consumed in all fabricated recipes was self-made by our laboratory.

### 2.2. Methods

The form-stable blends were synthesized by ultraviolet assisted hydrolysis method aiming to shorten the polycondensation time of MEMO and improve the yield of the products. The mechanism of designed fabrication may be divided into two steps, hydrolysis, directional adsorption and condensation, which is shown in Fig. 1. A typical synthetic process is described as follows: (1) 10 mL saturated solution of ET

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