Preparation and thermal properties of octyl, decyl, dodecyl and tetradecyl stearates as phase change materials for thermal energy storage

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ABSTRACT

A homologous series of *n*-alkyl stearates C_nS ($C_{17}H_{35}COO(CH_2)_{n-1}CH_3$, n = 8, 10, 12, 14) was synthesized as solid-liquid phase change materials (PCMs) by esterification of stearic acid with 1-octanol, 1-decanol, 1-dodecanol and 1-tetradecanol. Molecular structures of C_nS were confirmed by fourier transform infrared (FT-IR) and ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra. Differential scanning calorimetry (DSC) measurements revealed that the melting temperatures of C_nS were in the range of $21.4 \sim 44.4\,°C$ and increased with the increase in alkyl chain length. The latent heats of fusion were in the range of $165.8 \sim 191.1\,kJ\,kg^{-1}$. The comparable solidifying temperatures and latent heats of solidification were also observed. The phase change temperatures and latent heats changed little after repeated melting/solidifying cycles. Thermogravimetric analysis suggested that C_nS was thermally stable at temperatures up to $215\,°C$. The volumetric latent heat storage capacities of C_nS ranged from 146 to 159 MJ m^{-3}. The latent heat storage/release performance of C_nS in a ceramic cell suggested the potential application of the *n*-alkyl stearates for passive thermal energy storage to reduce the indoor temperature fluctuation.

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1. Introduction

Efficient utilization of latent heat for thermal energy storage in buildings has attracted widespread interests due to the advantage in reducing the indoor temperature fluctuation and the potential for reducing the CO_2 emissions from the combustion of fossil fuels [1,2]. Phase change materials (PCMs) could store thermal energy form the sunshine with much higher energy storage density when compared with the sensible heat storage materials [3]. In the building applications, the PCMs with melting points at around $18 \sim 30\,°C$ are preferred to provide thermal comfort through absorbing solar energy during the daytime and releasing the latent heat during the night [4]. Berroug et al. increased air temperature of greenhouse by $6 \sim 12\,°C$ at night time with less fluctuations through a passive storage wallboard impregnated with $CaC_{12} \cdot 6H_2O$ (melting point $29\,°C$) [5]. Based on thermal dynamics of PCM, Neeper pointed out that the maximum energy storage occurred when the melting point of PCM was close to the average room temperature in the passive solar building design [6]. The most frequently used $CaC1_2 \cdot 6H_2O$ for solar greenhouses suffered from super-cooling and sensitivity towards moisture [7]. Commercially available paraffins, which have been incorporated into composite wallboards [8], had disadvantages of low thermal conductivity and moderate flammability [9].

Besides salt hydrates and paraffins, fatty acids (e.g. myristic acid, palmitic acid, and stearic acid) have ever been recommended as potential PCMs for solar thermal energy storage in domestic water heating systems owing to the considerable latent heats of fusion [10]. However, their melting temperatures and latent heats decreased notably after repeated melting/solidifying cycles [11]. In order to obtain more stable PCMs, Li et al. synthesized a series of *di*-stearates by esterification of stearic acid with diols such as 1, 2-ethanediol, 1, 4-butanediol, 1, 6-hexanediol, 1, 8-octanediol and 1, 10-decanediol [12,13]. Sari et al. prepared a wide variety of mutli-stearates by esterifying ethylene glycol, glycerol, erythritol, xylitol and mannitol with various fatty acid chlorides [14–18]. Aydin et al. obtained high-chain fatty acid esters through esterification reaction between long-chain fatty alcohols (1-hexadecanol or 1-tetradecanol) and fatty acids (such as 1-eicosanoic acid) [19–21]. In addition, ethylene dilauroyl, dimyritoyl, and dipalmtiyol amides have also been derived from the respective carboxyl chlorides for the purpose of thermal energy storage [22]. These reported compounds exhibited superior thermal properties and reliability in terms of low temperature thermal storage through the phase change.

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Although melting temperatures and latent heats of fusion of methyl, ethyl and butyl stearates have been reported [23], thermal properties of n-alkyl stearates with longer alkyl chains as latent heat storage materials remain unexplored. With a view to investigating potential of octyl, decyl, dodecyl and tetradecyl stearates as PCMs, n-alkyl stearates (C_nS) were derived from fatty alcohols containing $8 \sim 14$ carbon atoms and the thermal storage/release performance was evaluated in this research. The melting temperatures and latent heats of fusion were found to be in the range of $21.4 \sim 44.4\,°C$ and $165.8 \sim 191.1\,kJ\,kg^{-1}$, respectively. Phase change temperatures and latent heats of C_nS changed by less than 3.2% after 1000 melting/solidifying cycles. The volumetric latent heat storage capacities of C_nS lay between 146 and $159\,MJ\,m^{-3}$. Stable latent heat storage/release of C_nS in a ceramic cell suggested the potential to construct PCM wallboards for thermal energy storage applications.

2. Experimental

2.1. Materials

Thionyl chloride (96%), 1-octanol ($\geq$99%), 1-decanol ($\geq$97%), 1-dodecanol ($\geq$98%), 1-tetradecanol ($\geq$99%) and other solvents were obtained from Chengdu Changzheng Co. Ltd. Stearic acid ($\geq$98.5%) was obtained from Sigma Company. All of the chemical materials were used without further purification.

2.2. Instrumentation

The ^1H nuclear magnetic resonance (^1H NMR) spectra were measured by using a Bruker AV II-600 spectrometer. The fourier transform infrared (FT-IR) spectra were obtained with the use of PerkinElmer Spectrum Two L1600300 spectrometer in the wavenumber range of 4000–500 cm^{-1}. The differential scanning calorimetry (DSC) measurements were conducted on a TA Q200 DSC under a nitrogen atmosphere at a constant heating/cooling rate of $2\,°C\,min^{-1}$. The peak temperatures of DSC curves were recorded as the phase transition temperatures. The latent heat of samples was determined by numerical integration of the area of the phase transition peak [24]. The uncertainty of the DSC data was estimated by repeating the measurement 3 times. The thermogravimetric analyses were performed using a TA instrument Netzsch TGA 209C at a heating rate of $10\,°C\,min^{-1}$. The onset temperature of weight loss during the heating process was reported as the decomposition temperature (T_d). The thermal cycling (1000 melting/solidifying cycles) was performed using Bio-Rad C1000 thermal cycler to evaluate thermal stabilities of C_nS.
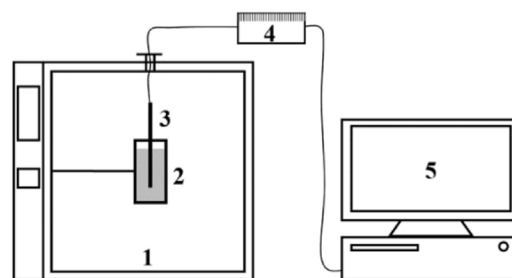

Fig. 1. Experimental set-up for the thermal storage/release characterization (1-thermostat; 2- ceramic cup; 3- thermocouple; 4-data logger; 5-computer).
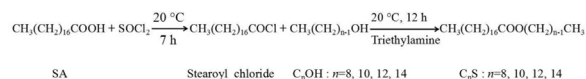

Fig. 2. The synthetic route of C_nS.

The samples were cycled between 10 and $50\,°C$ with isotherm of 1 min at the lowest and highest temperatures to assure complete phase change. The thermal conductivities were determined on a TC3000E thermal property analyzer (transient hot wire method; $0.001 \sim 10\,W\,m^{-1}\,k^{-1}$; accuracy: $\pm3\%$). The volumetric expansion during the phase change was characterized by a glass volume expander (accuracy: $\pm0.02\,ml$).

The latent heat storage/release of C_nS was characterized under an isothermal atmosphere. As shown in Fig. 1, the experimental set-up consisted of a thermostat (DZF-0B, accuracy: $\pm1\,°C$), a ceramic cell (inner diameter 46 mm; height 55 mm; wall thickness 2 mm) filled with C_nS (12 g for each sample), and a thermocouple (PT100, $-200 \sim 500\,°C$; accuracy: $\pm0.3\,°C$) immersed into the sample. The temperature of thermostat was set at $55\,°C$ for the heat storage measurements and at $7\,°C$ for the heat release measurements. The evolution of temperature was collected to evaluate the heat storage/release performance of C_nS.

2.3. Synthesis of C_nS

All reactions were carried out under a nitrogen atmosphere at room temperature. Stearoyl chloride was synthesized according to the procedure described previously [25]. The synthetic route of C_nS is shown in Fig. 2. Triethylamine was added to a solution of fatty alcohol ($C_8 \sim C_{14}$) in dichloromethane and the mixture was stirred for 30 min. Then a solution of stearoyl chloride in dichloromethane was added dropwise to the mixture. After stirring 12 h, the solvent was removed under reduced pressure. The residue was washed
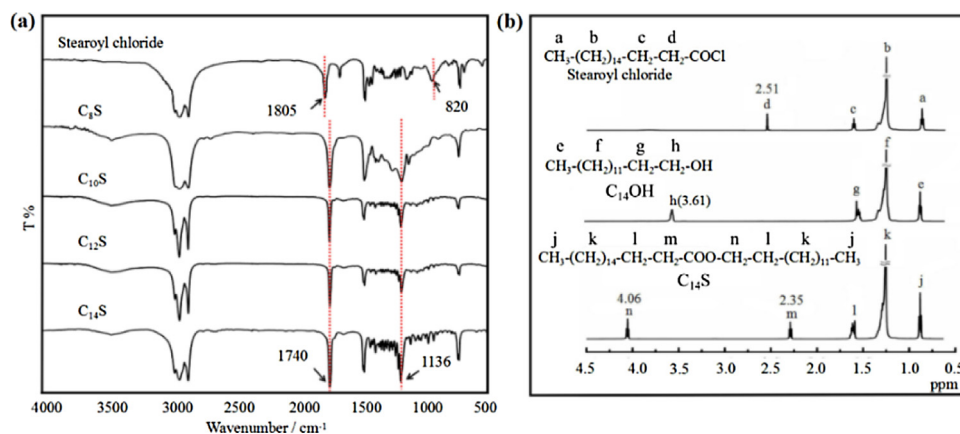

Fig. 3. FT-IR (a) and ^1H NMR (b) spectra of stearoyl chloride and C_nS.