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High-chain fatty acid esters of 1-hexadecanol for low temperature thermal energy storage with phase change materials

Ahmet Alper Aydın [a,*,1], Adnan Aydın [b]

[a] Chemical Engineering Department, Faculty of Chemical and Metallurgical Engineering, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey
[b] Department of Chemistry, Faculty of Arts and Sciences, Marmara University, 34722 Göztepe, Istanbul, Turkey

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ABSTRACT

High-chain fatty acid esters of higher alcohols have recently been investigated as novel organic phase change materials (PCM) for thermal energy storage. A series of high-chain fatty acid esters of 1-hexadecanol (cetyl alcohol) were prepared through esterification reaction between 1-hexadecanol and C10–C20 fatty acids with even carbon number in the absence of catalyst and under vacuum. FT-IR spectrometer, differential scanning calorimeter (DSC) and thermo-gravimetric analyzer (TGA) were intensively used for chemical and thermal analyses. Phase change temperature, enthalpy, specific heat (C_p), thermal decomposition and reliability after 1000 thermal cycles were obtained with necessary statistical data to clarify the thermal properties of the materials. The DSC analyses indicated that the melting temperatures of the high-chain fatty acid esters of cetyl alcohol were between 29 °C and 60 °C with phase change enthalpy above 185 kJ/kg. The results showed that these materials were favorable for low temperature heat transfer applications with superior thermal properties and reliability.

1. Introduction

Economical and effective thermal storage is the key element to adjust the energy demand imbalance of heat production and thermal energy storage systems are favorable to provide lower demand. Such systems have attracted the attention of many researchers due to the limited primary energy sources and increased cost of energy production [1,2]. Energy usage can be more efficient by improving the factors affecting the utilization of heat. Temperature level maintenance in living places [3,4], day and night usage of solar energy [5,6] and passive heat sinks created with the architectural design of the buildings [7,8] are useful tools to reduce the installed power. Thus, the dependence on heating power, which is mainly supplied from primary energy sources, decreases by utilization of renewable energy with the help of thermal energy storage.

Physically, thermal energy storage can be accomplished either by sensible heat storage or latent heat storage. However, the amount of heat stored as sensible heat is very limited compared to latent heat storage because latent energy density is higher and the deposition occurs at a constant temperature corresponding to the phase change temperature of the material.

Phase change materials (PCM) are substances with high latent heat of fusion, which are capable of storing or releasing large amounts of energy during melting and freezing at certain temperatures. During physical processes of thermal energy storage, temperature of a PCM rises initially as it absorbs heat; it performs like conventional storage materials. However, unlike conventional storage materials, when it reaches the temperature at which it changes phase, it absorbs large amounts of heat without a significant rise in temperature. When the ambient temperature around the material falls, the PCM releases its stored latent heat. They store much more heat per unit volume than conventional storage materials such as water, masonry or rock [9].

Over the past two decades, extensive efforts have been made to apply the latent heat storage method to solar energy systems, where heat is required to be stored during the day for use at night. Several researches have been conducted to determine the contribution of PCMs and to compare the solar energy storage systems based on latent heat and sensible heat storage. Chaurasia [10] conducted a comparative study with two identical storage units, one containing paraffin wax as the storage material, packed in a heat exchanger made up of aluminum tubes and another identical conventional storage unit with water. Both units have been separately charged by solar energy with the use of identical flat plate solar collectors. This research showed that the modified heat storage unit yielded more hot water next day in the morning as compared to the conventional storage unit. Zou et al. [11]

* Corresponding author. Tel.: +90 5323029298.
E-mail addresses: aydinal@itu.edu.tr, ahmetalperaydin@gmail.com (A.A. Aydın).
[1] Present Address: Department of Chemical-Technical Analysis and Chemical Food Technology, Technical University of Munich, Weihenstephaner Steig 23, D-85354 Freising, Weihenstephan, Germany.

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investigated the feasibility of using phase change emulsion (PCE) in heat transportation through piping system of a solar collector and reported that a system with PCE could reduce the volume of heat storage tanks compared to conventional water systems with less pumping power consumption.

Solar collectors, which perform as solar energy absorbing media and latent heat storage units have also been investigated. In these systems, solar energy is first stored in PCM layers in the solar collector and then it is transferred to the water circulating pipes located inside the PCM [12,13].

Solar thermal storage systems can also be designed according to the utilization of air as the heat transfer fluid. Air based solar heating systems have been intensively studied to determine the thermal performance and to make comments on suitable material selection [14,15]. Such systems are useful as crop dryer for aromatic herbs and medical plants, which are sensitive to direct exposure to sunlight. Bal et al. [15] mentioned as future perspective that hybrid systems with solar energy and thermal energy storage providing hot air at around 40–75 °C are needed for continuous air based solar heating systems.

The above mentioned researches briefly summarize the utilization of PCMs in different solar energy applications and they are mostly focused on utilization of paraffin waxes as thermal energy storage media with enthalpy greater than 200 kJ/kg and phase change temperatures between 50 ºC and 80 ºC. Paraffins are the most intensively used PCMs in applications due to their thermal reliability, insignificant supercooling tendency and non-corrosiveness. However, they are not the only organic material group with suitable thermal properties for thermal energy storage in low-temperature heat transfer applications such as deposition of solar energy, thermal insulation or temperature level maintenance.

The aim of this paper is to introduce six high-chain fatty acid esters of cetyl alcohol (1-hexadecanol) as novel organic phase change materials to be used in low-temperature heat transfer applications. The thermal properties of the synthesized materials are presented in terms of phase change temperature, enthalpy, specific heat capacity of solid and liquid phases, thermal reliability and thermal degradation with related statistical calculations. In addition to the presented thermal data, the effects of ester bond in the chemical structure on the thermal properties are also discussed in detail with comparison of high chain fatty acid esters of cetyl alcohol with fatty acids and saturated hydrocarbons, respectively.

2. Experimental

2.1. Materials

The high-chain fatty acid esters of cetyl alcohol were prepared and purified according to the published literature procedure [16] using 1-hexadecanol (99%), 1-decanoic acid (> 98%), 1-dodecanoic acid (> 99%), 1-tetradecanoic acid (99–100%), 1-hexadecanoic acid (> 99%), 1-octadecanoic acid (> 98.5%), 1-eicosanoic acid (> 99%) and n-tetratriacontane (98%) from Sigma-Aldrich. Acetone and ether were used as crystallization solvents for the purification of the final product of the synthesis. The reagents were used without further purifications.

2.2. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of the synthesized high-chain esters were recorded on Perkin Elmer FT-IR Spectrum 100 spectrometer with universal ATR accessory between 4000 and 600 cm^{-1} wavelengths.

2.3. Differential scanning calorimeter (DSC)

Perkin Elmer Jade DSC was used for the calorimetric analyses of the novel PCMs. The measurements were carried out under inert nitrogen atmosphere at 20 ml/min flow rate. All the DSC thermal analyses were conducted at 2 °C/min heating and cooling rate for the determination of phase change temperature and enthalpy. Specific heat values of solid and liquid phases were determined at 5 °C/min heating rate.

DSC analyses were conducted according to the ASTM standard test methods with designation numbers E 792-06 and D 2766-95, explaining the determination of enthalpies of fusion and freezing and specific heat of liquids and solids, respectively [17,18]. The temperature and heat calibration of the instrument was performed systematically with zinc and indium references prior to the analysis on each workday. Every presented DSC data in this paper is calculated according to the results of atleast 4 individual analyses in order to minimize the uncertainty.

2.4. Thermo-gravimetric analyses (TGA)

Perkin Elmer STA-6000 was used for the thermo-gravimetric decomposition of the novel PCMs with temperature, including the decomposition behavior, onset and 5% weight loss temperatures of the materials. The analyses were carried out under inert nitrogen atmosphere at 20 ml/min flow and 10 °C/min heating rates.

The analyses were conducted according to the general principles given in BS EN ISO 11358:1997 [19]. The weight and temperature calibrations of the instrument were performed using the reference weight and according to the sensor calibration of the instrument, respectively. The calibration of the instrument was performed systematically prior to the first analysis of each workday. Every presented TGA data in this paper is calculated according to the results of atleast 2 individual analyses.

2.5. DNA thermal cycler

In this research, Bio-Rad MJ Mini DNA thermal cycler was used to provide automated 1000 heating and cooling cycles in order to observe the thermal performance of each PCM. Each PCM was cycled in the temperature interval of 25 °C to provide complete phase change with one minute isothermal at the lowest and highest temperatures.

3. Results and discussion

3.1. The synthesis of High-chain fatty acid esters

Baykut and Aydın [16] reported that high-chain fatty acid esters of C10–C20 fatty acids could be synthesized with high reaction yields of final product up to 94 (w/w)% under vacuum and in the absence of catalyst. According to their given detailed procedure, it is simpler and more advantageous than Fischer esterification, which is the most commonly used method. Therefore, the given high-chain fatty acid esters of cetyl alcohol in Table 1 were synthesized via the method of Baykut and Aydın [16].

The FT-IR spectra of the synthesized esters show that the final products do not contain unreacted alcohol and fatty acid impurities. The crystallization of high-chain fatty acid esters with acetone and ether is effective to remove unreacted impurities. The absence of oxygen–hydrogen stretching vibrations of fatty acid and alcohol between 2500 and 2700 cm^{-1} and 3230 and 3550 cm^{-1} indicates that the final products are free of any