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A eutectic mixture of galactitol and mannitol as a phase change material for latent heat storage

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ABSTRACT

The thermophysical properties of mixtures of galactitol and mannitol were examined via differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD) analysis. The aforementioned sugars were found to form a eutectic mixture at a 30:70 molar ratio of galactitol and manntitol, and displayed a melting point of 153 °C while maintaining a high latent heat of fusion (ΔH_{fus} = 292 J g^{-1}). The XRD data revealed that the eutectic mixture contained the α, β, and δ forms of mannitol with the δ form being the major component. By varying the temperature ramp rates utilized in the DSC measurements from 0.5 °C min^{-1} to 20 °C min^{-1}, the heat of crystallization as well as the crystallization temperature increased (c.f., ΔH_{crys}: 64 J g^{-1} → 197 J g^{-1}; T_c: 68 °C → 105 °C). In addition, the temperature and the enthalpy of crystallization were also improved by up to 34% through the addition of small quantities (up to 0.5 wt%) of nucleating agents, such as graphite powder or silver iodide. After 100 heating/cooling cycles under an atmosphere of nitrogen, the heat of fusion of the eutectic mixture decreased by only 4% with no change in the melting point, and the mixture appeared to be chemically stable according to a Fourier transform infrared (FT-IR) spectroscopic analysis. Collectively, these data indicate that the eutectic mixture exhibits excellent cyclic stability under ambient atmospheres and offers potential for use in thermal energy storage applications.

1. Introduction

High-density 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 [1]. To be practical, TES systems require storage materials that display (1) high energy densities, (2) a practical phase change temperature, and (3) high durability. Phase change materials (PCMs), which absorb and release thermal energy when they melt and solidify at nearly constant temperature during the phase transition, offer the potential for meeting the aforementioned requirements. Indeed, paraffin, fatty acids, sugar alcohols and salt hydrates have been used or investigated as PCMs for thermal storage applications [2–8]. The sugar alcohols such as threitol, allitol, iditol, erythritol, mannitol, dulcitol and their eutectic mixtures are particularly promising candidates for use in TES applications due to their broad range of melting temperatures, high volumetric energy densities, non-corrosive nature, and high thermal stabilities [9]. As one of the widely studied sugar alcohol based PCMs, erythritol melts between 117 and 120 °C and displays a heat of fusion that ranges between 340 and 344 J g^{-1} [7,10–12]. The stereoisomers, galactitol and mannitol, have also been investigated as PCMs (see Table 1 for a summary of their thermal data).

Recently, Solé et al. explored the potential of using myo-inositol, galactitol, and mannitol as PCMs via differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy [13]. As part of that study, myo-inositol was found to undergo polymorphic changes between 50 °C and 260 °C, and displayed a relatively high cyclic thermal stability when analyzed between 150 °C and 260 °C. For comparison, galactitol showed relatively poor thermal cyclic stability as the crystallization temperature decreased to 60 °C from its initial value of 120 °C after 18 cycles, and eventually no crystallization was observed after the 19th cycle of analysis. Similarly, the enthalpies of heating and crystallization displayed by D-mannitol decreased by 30% and 50% after 20 and 50 thermal cycles, respectively. FT-IR spectroscopic

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Table 1
A summary of thermal data for various sugars.

Type	Melting point (°C)	Heat of fusion (J g^{-1})	Polymorphic phase	Reference
Galactitol (or dulcitol)	179.8	246.4	–	[13]
	180.3	267.9	–	
	187.2	357.4		[14]
	186–187	330.0	–	[15]
Mannitol	162.2	326.8	–	[8]
	166.0	308.2		[14]
	166.0	290.0	–	[15]
	167.0	246.0	β	[16]
	157.0	243.0	δ	
	166.0	294.0	β	[17]
	166.0	286.3	α	
	155.0	295.1	δ	
	165.0	338.0	β	[18]
	165.6	302.2	α	[19]
	165.4	297.3	β	
	164.6	280.2	γ	
	165.4	279.1	δ	
	164.1	264.3	κ	

analysis of galactitol and D-mannitol after the aforementioned thermal cycles, which were performed under air, indicated that the sugars underwent undesired oxidation to derivatives that displayed relatively low heat capacities.

In general, sugar alcohols with high heats of fusion often exhibit high melting temperatures, which limits the choice of heat transfer fluids to be used in conjunction with sugar alcohol based thermal storage media. Hence, there is a need to develop sugar-based PCMs that display relatively low melting temperatures without reducing the heats of fusion.

Herein, we report the thermophysical properties of galactitol, mannitol, and their mixtures, and explore their potential for use as PCMs in medium temperature range TES systems. We also study the cyclic, thermal, and chemical stabilities of a eutectic mixture of galactitol and mannitol using differential scanning calorimetry (DSC) and FT-IR spectroscopy. The use of various additives to suppress the subcooling of the eutectic mixture was also explored.

2. Materials and method

2.1. Preparation of sugar alcohol mixtures

Galactitol (or Dulcitol) (99+%, Alfa aesar) and β-*D*-mannitol (99%, Acros) were used as received. In general, galactitol and mannitol were combined such that the resulting mixture contained 10, 20, 30, 40, 50, 60, 70, 80, 90, or 100 mol% of mannitol. In a typical procedure, a round-bottomed flask containing a mixture of galactitol and mannitol was immersed in a pre-heated silicone oil bath maintained at 200 °C. The mixture was then stirred for 15 min to melt both sugars. The resulted liquid mixture was slowly cooled to room temperature. In cases where a nucleating agent (see below) was used, the agent was added to the eutectic mixture of galactitol and mannitol, followed by heating above its melting point while being stirred.

2.2. Differential scanning calorimetry (DSC)

DSC studies were performed using a Mettler Toledo DSC823e. Heating and cooling rates of 0.5–20 °C min^{-1} were typically employed. All experiments were performed under nitrogen with a flow rate of 50 mL min^{-1}. All weight measurements were accurate up to 0.001 mg in a sealed aluminum cell with or without small piercings, where necessary. The DSC was calibrated for heat flow and temperature using indium and zinc standards. All samples were pre-heated to 80 °C, allowed to cool down to their crystallization points, and then reheated for data collection. The melting points and heats of fusion were obtained from the second heating cycle and the average value of three independent DSC experiments was used.

2.3. Thermogravimetric Analysis (TGA)

The thermal stabilities of sugar alcohols and the aforementioned eutectic mixture was analyzed using a TA instruments (Q50) thermogravimetric analyzer at a scan rate of 10 °C min^{-1} under an atmosphere of nitrogen. A typical sample size of 8–10 mg was used for the TGA analyses.

2.4. FTIR spectroscopy

Attenuated total reflection infrared (ATR-IR) spectra were recorded using a ThermoScientific Nicolet iS10 ATR/FT-IR spectrometer attached to an attenuated total reflection (ATR) apparatus. A resolution of 4 cm^{-1} and the average of 120 automated scans from 400 to 4000 cm^{-1} were used to obtain the IR spectra.

2.5. Powder X-ray diffraction analysis

The sugar alcohol based mixtures were studied used powder X-ray diffraction in conjunction with DSC to characterize the physical state of the material. X-ray powder diffraction (XRPD) profiles of the samples were obtained using a Philips PW 1050/70 PW 1710 diffractometer fitted with a scintillation counter and Cu Kα radiation source (wavelength = 0.15418 nm). The divergence and detector silts were of 0.3° and 0.18° aperture, respectively. Data were collected between 5° and 50° of $2-\theta$ in a step mode using a step size of 0.02° of $2-\theta$ and collecting time of 1 s per step.

2.6. Thermal conductivity measurements

The through-thickness thermal diffusivity of cast molded samples of thickness 2 mm and diameter 10 mm was measured using a laser flash system (Netzsch LFA-457 micro flash). We have calculated κ_{PCM} using the eutectic mixture's specific heat (C_{PCM}), as measured using a DSC (Netzsch DSC-404 F1 Pegasus), and the measured mass density (ρ_{PCM}) to obtain the thermal conductivity as $\kappa_{PCM} = \alpha_{PCM}\rho_{PCM}C_{PCM}$.

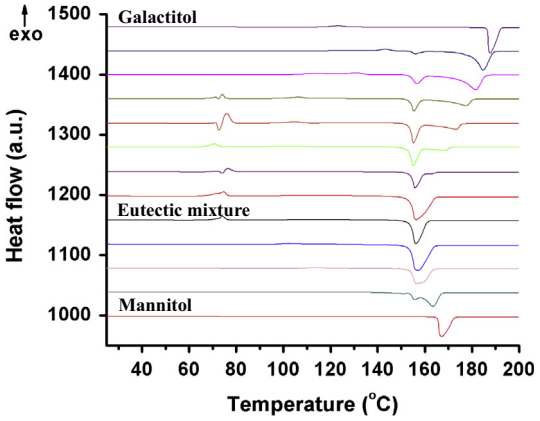

Fig. 1. DSC melting curves of galactitol, mannitol, and their mixtures. The mannitol content in the mixture is 0, 10, 20, 30, 40, 50, 60, 65, 70, 75, 80, 90, 100 mol%, respectively, for the 13 curves in the order from the top to the bottom. A ramp rate of 10 °C min^{-1} was employed for these experiments.