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Estimation of thermal endurance of multicomponent sugar alcohols as phase change materials

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HIGHLIGHTS

- Single or multi-component sugar alcohols were selected as phase change material.
- Mannitol, dulcitol, and inositol were selected as base-components.
- We estimated their thermal endurance using constant temperature kinetics.
- The thermal endurance of the sugar alcohols increased as the lowering of the melting temperature.
- Especially, dulcitol/mannitol eutectic mixture showed the longest degradation period.

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ABSTRACT

This study investigates the thermal endurance of sugar alcohols and their eutectic mixtures as phase-change materials (PCMs). Three sugar alcohols (mannitol, dulcitol, and inositol) and their eutectic mixtures were selected as the PCM candidates. First, the thermophysical properties of the single- and multicomponent sugar alcohols were characterized using differential scanning calorimetry. Second, the thermal endurance of the PCM candidates was estimated by constant-temperature kinetics based on the degradation of the latent heat of the PCM candidates. The results showed that mannitol, dulcitol, inositol, and their eutectic mixtures had melting points and latent heats of over 423 K and 200 kJ/kg, respectively. The kinetic analysis of the PCM candidates showed that the first-order reaction rate equation was suitable for analyzing the degradation of the latent heat of the sugar alcohols. The degradation periods increased with decrease of melting temperatures of each sugar alcohol. In particular, the dulcitol/mannitol eutectic mixture showed the longest degradation periods of 9817 ks, which is 5.68 and 6.85 times greater than those of pure mannitol and dulcitol, respectively. These observations indicated that eutectic mixtures of sugar alcohols were promising and alternative PCM candidates in the 373–473 K temperature range.

1. Introduction

Latent heat storage (LHS) is one of the promising methods to utilize unused thermal energy. LHS is based on the storage or release of latent heat when a phase-change material (PCM) undergoes a phase transition from a solid to liquid or vice versa. This simple principle provides great advantages such as large heat storage density with a smaller temperature difference between storing and releasing heat, and repeatable utilization. Various aspects of investigations, developments, and applications of LHS have found reflection in previous reviews and monographs [1–6].

Recently, much attention has been paid to the development of new PCMs at temperatures of around 473 K. The largest amount of industrial waste heat is typically generated at this temperature range. For example, according to the report of The Energy Conversion Center, Japan, the exergy of industrial waste heat at the temperature range 373–523 K contributes to 56% of the total exergy [7]. Moreover, the heat-source applications in this temperature range include applications such as in steam generators, heat pumps, and thermally driven refrigerators.

Single-component sugar alcohols [8,9] and their esters [10–12] are reported as promising PCMs from viewpoints of large heat capacity and non-toxic. Especially, erythritol, a sugar is the most promising PCM in the aforementioned temperature range. Erythritol has a suitable meting point (T_m) and large latent heat (L) of

Abbreviations: DSC, differential scanning calorimetry; LHS, latent heat storage; PCM, phase-change material.

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Nomenclature

E_a	Activation energy (kJ mol^{-1})
L	Latent heat (kJ kg^{-1})
L_0	Latent heat of samples before heat treatment (kJ kg^{-1})
L_t	Latent heat of the samples after heat treatment for t min (kJ kg^{-1})
$L_{t,\deg}$	Degrading latent heat after holding at T_h for t min. (kJ kg^{-1})
K	Reaction rate constant (min^{-1})
lnA	Exponential prefactor (−)
t	Time (min)
T	Temperature (K)
T_h	Holding temperature (K)
T_m	Melting point (K)
α	Degradation level (−)

391 K and 340 kJ/kg, respectively [9]. It is nontoxic and noncorrosive for metallic vessels [13]. Therefore, it has been used in various applications such as solar cookers [14,15], waste-heat transportation [9,16–18], and as a heat source for single-effect absorption chillers [17].

Because the T_m of erythritol is relatively low to utilize the heat source at around 473 K, sugar alcohols other than erythritol have been studied as new PCM candidates. Mannitol, in particular, has a T_m of about 440 K, which is higher than erythritol, and large L values [9]. In addition, it is also nontoxic and noncorrosive for metallic vessels [13]. Therefore, mannitol can offer more efficient utilization of unused thermal energy than erythritol. For example, mannitol can be used as a heat source for solar cooling and refrigerating applications [19]. However, some studies have identified the low thermal endurance of mannitol as an obstacle to its practical applications [13,20,21].

One method to improve the thermal endurance of mannitol is by controlling its T_m by impregnating the PCM into nanosized pores. In a previous study [22], we investigated the control of T_m and improvement of thermal endurance of D-mannitol by vacuum impregnation of the PCM into the nanosized pores of SiO_2 grains. The results showed that the T_m shifted to lower temperatures with smaller pore diameter (D_P) of the composites. In particular, a low T_m of 413 K was observed for the PCM/SiO_2 composite with a D_P of 11.6 nm. Moreover, the thermal degradation period of the PCM/SiO_2 composite with a D_P of 11.6 nm was 13 times longer than that of the pure PCM at a holding temperature that was 10 K higher than the individual T_m.

Another way of controlling the T_m of sugar alcohols is by mixing the PCMs. It has been reported that the T_m value of a PCM changes on preparing a eutectic mixture [23–26]. In the case of sugar alcohols, Hidaka et al. [8] proposed the erythritol–polyalcohol mixtures as PCMs for heat storage in the temperature range 353–373 K for a water-supply system. However, there are no studies on the thermal endurance of these eutectic mixtures.

The purpose of this study was to estimate the thermal endurance of sugar alcohols and their eutectic mixtures as PCMs by constant-temperature kinetics. We selected three sugar alcohols, namely mannitol, dulcitol, and inositol, as PCM candidates and prepared three eutectic mixtures. The thermal endurance of these eutectic mixtures was examined by constant-temperature kinetics based on the L of the PCMs. The thermophysical properties of the samples were measured by differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

Three sugar alcohols, namely mannitol ($C_6H_{14}O_6$, 99.0% purity, T_m = 440 K, Kanto Chemical), dulcitol ($C_6H_{14}O_6$, 99.0% purity, T_m = 460 K, Wako Pure Chemical), and inositol ($C_6H_{12}O_6$, 99.0% purity, T_m = 497 K, Wako Pure Chemical), were selected as the PCM candidates of the eutectic mixtures. Because these materials possess a T_m of over 423 K, they were expected to utilize the heat source at a temperature higher than that of erythritol (T_m: 391 K). Three eutectic mixtures (inositol/mannitol, dulcitol/mannitol, and inositol/dulcitol/mannitol) were prepared by mixing the alcohols under ambient conditions. Table 1 lists the mixing ratios of eutectic mixtures used in this study. The mixing ratios were based on the previous report by T. Nagasaka [27]. The report [27] experimentally decided mixing ratios of the eutectic mixtures of erythritol, mannitol, dulcitol, and inositol. In addition, phase diagrams of these eutectic mixtures were thermodynamically calculated.

2.2. Thermal analysis

The T_m and L values of mannitol, dulcitol, inositol, and their eutectic mixtures were measured by DSC using an open Al crucible under nitrogen atmosphere. The DSC recordings were obtained from room temperature to 523 K at a heating or cooling rate of 2 K/min. To reduce the measurement errors, all the samples were completely melted and then cooled to room temperature prior to the measurement.

2.3. Kinetics of thermal degradation

The thermal degradation characteristics of pure PCM and eutectic mixtures were evaluated by constant-temperature kinetics [28–30] based on the L values measured by DSC. The DSC method for the constant-temperature based on the L has advantages that it can evaluate the thermal degradation characteristics of PCMs using closed crucibles PCM is usually packed and used in closed systems such as capsules and tanks, therefore, the thermal degradation characteristics of PCM should be evaluate under closed systems. In a previous study, we measured the thermal degradation characteristics of D-mannitol as PCM using the same method and obtained reasonable results [22].

Prior to the measurement, the samples were packed in a closed stainless steel crucible under an argon atmosphere to prevent the degradation from oxidation. In this study, the thermal degradation characteristics were evaluated under isothermal conditions. A degradation level, α, was defined according to Eq. (1), which uses the ratio between the L before and after the isothermal heat treatment:

$$\alpha = 1 - \frac{L_t}{L_0} \tag{1}$$

where L_t is the latent heat of the samples after heat treatment for t min, and L_0 is their latent heat before the heat treatment.

First, the samples were heated at a rate of 10 K min^{-1} to different temperatures over T_m for the individual DSC measurements. Then,

Table 1
Mixing ratios of eutectic mixtures used in this study.[27]

Material	Mol fraction [mol]		
	Mannitol	Dulcitol	Inositol
Inositol/mannitol	0.771	–	0.229
Dulcitol/mannitol	0.697	0.303	–
Inositol/dulcitol/mannitol	0.557	0.237	0.206