



The experimental phase diagram study of the binary polyols system erythritol-xylitol



Saman Nimali Gunasekara^{a,*}, Justin NingWei Chiu^a, Viktoria Martin^a, Peter Hedström^b

^a Department of Energy Technology, KTH Royal Institute of Technology, Brinellvägen 68, 100 44 Stockholm, Sweden

^b Department of Materials Science and Engineering, KTH Royal Institute of Technology, Brinellvägen 23, 100 44 Stockholm, Sweden

ARTICLE INFO

Keywords:

Phase change material (PCM)
Erythritol-xylitol phase diagram
Temperature-history (T-history) method
X-ray diffraction (XRD)
Field-emission scanning electron microscopy (FESEM)
Eutectic

ABSTRACT

A comprehensive phase diagram for the binary polyols system erythritol-xylitol has been mapped with a transparent characterization approach. Here, the phase equilibrium of the system has been studied experimentally using a combination of methods: Temperature-history (T-history), X-Ray Diffraction (XRD), and Field-Emission Scanning Electron Microscopy (FESEM), and linked to Tammann plots. Existing literature has previously shown the system to be a non-isomorphous type forming a simple eutectic, by combining experimental data with theoretical modelling. The present investigation shows that the system's phase diagram is a partially isomorphous type forming a eutectic, but not a non-isomorphous type forming a simple eutectic. Here, the eutectic was found within 25–30 mol% erythritol and at 77 °C, which differs from the previous studies identifying the eutectic respectively at 25 or 36 mol% erythritol and at 82 °C. The reasons for the differences are hard to deduce since the research approach is not presented as fully transparent from the past studies. In the present study, only the temperature-composition plot of the first melting (of the two components in a physical mix, but not of a single blend) indicated the shape of a simple eutectic in a non-isomorphous system. The cycles after the first melting in contrast started from the real blend, and displayed eutectic and solid-solid phase changes in T-history. These were verified as forming solid solutions with XRD and FESEM. This eutectic melts at a temperature suitable for low-temperature solar heating, but displayed glass transition, supercooling, and thermally activated degradation, thus affecting its practical aspects as a PCM.

1. Introduction

Energy storage is needed for the effective utilization and management of energy. In that, thermal energy storage (TES) is one alternative. TES enables load shifting of thermal energy demand [1–4], with opportunities for cost-benefits depending on the type of supply system. Also, TES can alleviate fossil fuel-based heating and cooling demands by storing excess thermal energy from industries and power plants (e.g. [5–10]), and thus mitigating CO₂ emissions [11,12]. Such stored heat or cold can balance the energy mismatch between these sources and demands at different locations and time (e.g. [13–17]). Phase change materials (PCMs) are attractive for TES, with a higher storage density as

compared to sensible TES, and the ability to regulate temperatures within a narrow window. To integrate renewable energy sources, particularly such as solar heating and cooling, PCMs are an effective storage choice [18,19]. The challenges in PCM design include cost, and accomplishing a material with robust functionality while avoiding issues like supercooling and phase separation. Material blends could be tailored as PCMs for specific applications. In addition, if the blends e.g. come as industrial by-products, those could prove to be cost-effective PCMs. However, blends come with complex phase changes. Here, a phase equilibrium study, including establishing the phase diagram, is the key to find compositions that have sharp, reversible¹ phase change and no phase separation (e.g. congruent melting compositions, and

Abbreviations: Cu-ETP, electrolytic copper; DSC, Differential Scanning Calorimetry; DTA, Differential Thermal Analysis; Er, Erythritol; FESEM, Field-emission Scanning Electron Microscopy; FT-IR, Fourier Transform Infra-Red Spectroscopy; HT, High-temperature; HTXRD, High-temperature X-Ray Diffraction; IR, Infra-Red; IRT, Infra-Red thermography; L, liquidus; NA, Not available; NPG, Neopentyl glycol; PCM, Phase Change Material; PER, Pentaerythritol; PLM, Polarized Light (thermo-) Microscopy; PTFE, Polytetrafluoroethylene; RT, Room-temperature; RTD, Resistance Temperature Detectors; RTXRD, Room-temperature X-Ray Diffraction; S, solidus; SEM, Scanning Electron Microscopy; S_{Er}, a solid solution of erythritol; S-S, solid-solid / solvus (in the phase diagram); S-SPC, solid-solid phase change; S_{Xy}, a solid solution of xylitol; TE, Trimethylol ethane; TEM, Transmission Electron Microscopy; TES, Thermal Energy Storage; TGA, Thermogravimetric Analysis; T-history, Temperature-history; TPS, Transient Plane Source; XRD, X-Ray Diffraction; Xy, Xylitol

* Corresponding author.

E-mail addresses: saman.gunasekara@energy.kth.se (S.N. Gunasekara), justin.chiu@energy.kth.se (J.N. Chiu), viktoria.martin@energy.kth.se (V. Martin), pheds@kth.se (P. Hedström).

¹ i.e., a phase change (of e.g. solid-liquid change) that undergoes complete transformation for any number of cycles

<http://dx.doi.org/10.1016/j.solmat.2017.08.005>

Received 1 April 2017; Received in revised form 1 August 2017; Accepted 3 August 2017
0927-0248/© 2017 Elsevier B.V. All rights reserved.

Nomenclature*Symbols*

A	Heat transfer area (m^2)
c_p	Specific heat at constant pressure ($\text{kJ}/(\text{kg}\cdot\text{K})$)
Δh	Enthalpy change (kJ/kg or kJ/mol)
dT	Temperature difference (K , $^\circ\text{C}$)
Δt	Time difference (s)
k_1	Constant (W/K)
k_2	Constant (W)
lmtd	Logarithmic mean temperature difference (K , $^\circ\text{C}$)
m	Mass (g)
Q	Heat (J)
\dot{Q}	Heat transfer rate (W)

SSTT	Stainless steel test tube
t	Time (s)
T	Temperature ($^\circ\text{C}$)
U	Overall heat transfer coefficient ($\text{W}/(\text{m}^2\text{K})$)

Subscripts and superscripts

E	eutectic
M	melting
SS	stainless steel
S-S	solid-solid
Intm	intermediate
Tot	total
R	reference

eutectics if no supercooling occurs [20]). In addition, compositions already known to supercool and phase separate can be avoided (e.g. peritectics [20]).

Polyols (or poly alcohols, i.e., alcohols containing more than one hydroxyl group) are attractive candidate PCMs (e.g. [21–35]), with low to moderate melting temperatures and considerable melting enthalpies (~ -15 – 245 $^\circ\text{C}$ and 100 – 413 kJ/kg) [29], renewable origin, and non-toxic nature [29,36]. Their material challenges include: glass transition (e.g. xylitol, sorbitol and maltitol [29,37–40]); thermally activated degradation (i.e., browning and thickening [29] or tanning [34] in e.g. erythritol, xylitol, myo-inositol, galactitol and D-mannitol [13,27,29,34,41]); large supercooling (e.g. erythritol [29] and mannitol-galactitol [31]); and considerable hysteresis (e.g. myo-Inositol, galactitol, and D-mannitol [27]). Polyols are prone to metastabilities as well, which is also an important TES design fact. A predominant metastable solid-solid phase was reported e.g. for erythritol at 102 – 112 $^\circ\text{C}$ with an enthalpy of 255 – 314 kJ/kg [28,29,42], and for xylitol at 61 – 61.5 $^\circ\text{C}$ [43,44] (and the enthalpy is unknown).

A number of polyol blends have also been studied assessing their phase equilibrium in the PCM-context [21–23,31,38,45–50], including the erythritol-xylitol system [21,22,33]. These have identified: numerous eutectics (in erythritol-xylitol, erythritol-sorbitol, sorbitol-xylitol, adonitol-erythritol, arabitol-erythritol, arabitol-xylitol, erythritol-dulcitol, xylitol-mannitol, adonitol-mannitol, and mannitol-dulcitol [21,22,31–33,38,47–49]); some monotectics (in D-sorbitol-D-mannitol, xylitol-dulcitol, xylitol-D-mannitol, and adonitol-dulcitol [38,46–48]); and a co-crystalline behavior (in xylitol-D-sorbitol and sorbitol-mannitol [47]). Among certain polyols, miscibility gaps among components with dissimilar structures (e.g. Pentaerythritol (PER)-neopentyl glycol (NPG) and pentaglycerine (PG)-NPG) and solid solubility among polyols with similar crystal structures (e.g. PER-PG) have also been observed [46]. The ring-structured polyols (e.g. mannitol, dulcitol and inositol) were found to improve the thermal endurance of eutectic polyol blends involving them [32].

The focus in this paper is on the system erythritol-xylitol, raising hopes for suitable PCM-blends in the temperature range 60 – 120 $^\circ\text{C}$ which is highly relevant for (solar) heating applications. Recently, the phase diagram for this system was concluded to be containing a simple eutectic in a non-isomorphous system,² based on phase equilibrium studies using a combination of methods (Differential Scanning Calorimetry (DSC) [21,33], Infra-red Thermography (IRT)³ [33], Polarized

Light Microscopy (PLM), X-Ray Diffraction (XRD) [21], and thermodynamic modelling [21,33]). However, in another study, the same system was analyzed experimentally employing the Temperature-history (T-history) method [22], which showed that in addition to a possible eutectic, solid-solid and other complex phase changes were present. It was then concluded that the thermal property evaluation alone was insufficient to explain these complexities as well as the disparities found between the studies.

Comparing these erythritol-xylitol investigations, some of the presented phase diagrams are preliminary, for lacking physical characterizations [22,33], and for containing a wide dispersion in the liquidus points [33]. The final erythritol-xylitol phase diagram was concluded by evaluating, three chosen melting cycles (involving seeding during cooling) in the T-history study [22], or an unspecified number of cycles in the other studies [21,33]. Diarce et al. [21] only detail the use of: one melting in DSC with no indication of seeding; and in PLM the first melting, a seeding induced freezing, and another melting [21]. There, the PLM was used to justify the use of the offset temperature of the DSC specific heat (c_p) melting peak as the liquidus, and to determine a slow heating/cooling rate to maintain thermal equilibrium [21]. The DSC was used to find the liquidus of the system using the slow rate defined by PLM [21]. With no new or disappearing peaks observed in XRD at room temperature, the system was concluded to be immiscible in the solid-state, which was then used as a condition in the theoretical modelling [21]. Del Barrio et al. [33] derived their phase diagrams primarily using the IRT method, and simplified theoretical modelling assuming ideal liquid solutions. They [33] only detail: melting the powders externally and pouring a droplet of this into the IRT plate cavities; cooling the droplet at room temperature till crystallization; and evaluating the melting of this solid in the IRT. The DSC was only used to ‘refine’ the eutectic by examining the thermograms around its composition, and to determine the melting enthalpies of the pure components and the blends [23,33]. There, for the samples tested in the DSC, only the first melting was detailed [23].

Given these procedural and results inconsistencies in literature, with the main objectives of comprehensively determining the erythritol-xylitol phase diagram, and to explain the complexities observed, this paper presents an experimental phase equilibrium analysis of the erythritol-xylitol system. For that, a combination of experimental methods have been used: the T-history method (coupled with a Tammann plot assessment); X-Ray Diffraction (XRD); and Field-Emission Scanning Electron Microscopy (FESEM). Here, including the cycled behavior of the system for at least three cycles was also prioritized. The thermal conductivity of the pure components and some blends are also presented, determined using the Transient Plane Source (TPS) method with a Hot Disk Analyzer.

² i.e., a non-isomorphous system (a system completely immiscible at the solid state) with just a single eutectic.

³ In the IRT method, blend droplets deposited on small cavities on an aluminum plate mounted on a heating/cooling stage are imaged using an IR camera, after which the IR emissivity changes during heating are mathematically interpreted to estimate the phase change temperatures [23].

Download English Version:

<https://daneshyari.com/en/article/6456668>

Download Persian Version:

<https://daneshyari.com/article/6456668>

[Daneshyari.com](https://daneshyari.com)