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Manipulation of phase transition temperatures and supercooling of sugar alcohol based Phase Change Materials (PCMs) by urea

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1. Abstract

In this work we have investigated the possibility to change thermal characteristics of the sugar alcohols erythritol and mannitol by use of urea as additive. The results show that even small amounts of urea have a great influence on the thermal properties of the sugar alcohols, which in turn implies large structural differences between the different compositions. For both sugar alcohols both smaller and higher fractions of urea result in two melting peaks, whereas a eutectic composition is obtained at intermediate urea fractions. However, not all compositions undergo crystallization on cooling.

Keywords: Sugar alcohols, melting, crystallization, supercooling, urea, differential scanning calorimetry (DSC)

2. Introduction

Heat storage solutions is seen as one possible solution for increasing the energy efficiency and reducing the energy consumption in, among others, the building sector. One way to store heat is to use the latent heat of phase change materials (PCMs). Previously we have studied different characterization methods on commonly used salt hydrates [1, 2]. Another group of materials of great interest as PCMs is the sugar alcohols, which are organic non-toxic, non-corrosive, biodegradable and inexpensive compounds. However, even if the phase transition enthalpy in general is high, there are two main problems with sugar alcohols that have to be solved before they can be used as PCMs for various building applications [3]. One problem is the generally large difference between the melting and crystallization temperatures, i.e. the supercooling. The other one is that the phase transitions normally occurs at rather high temperatures. Previously it was shown that the addition of urea can reduce the melting temperature of various sugar based materials [4]. In this study we have therefore, by use of differential scanning calorimetry (DSC), investigated the possibility to lower the melting temperature while reducing the supercooling of erythritol and mannitol by use of this additive.

3. Results and discussion

In table 1, the characteristic melting and crystallization temperatures and the melting enthalpy are shown for the pure sugar alcohols erythritol and mannitol. As can be observed, both the melting and crystallization temperatures as well as the supercooling ΔT are high. For erythritol $\Delta T \sim 100$ °C and for mannitol $\Delta T \sim 50$ °C, respectively. Note here that urea has a melting temperature of about 135 °C.

Table 1. Characteristics of the pure sugar alcohols

Sugar alcohol	T_{melt} (°C)	T_{cryst} (°C)	ΔH_{melt} (J/g)
erythritol	122	21	345
mannitol	167	118	330

Figures 1 and 2 show the DSC curves obtained for erythritol-urea (EU) and mannitol-urea (MU) blends of different weight fractions. As can be observed, the thermal scenario is rather complex and even smaller amounts of urea have a great influence on both the melting (left panels) and crystallization (right panels) of both sugar alcohols.

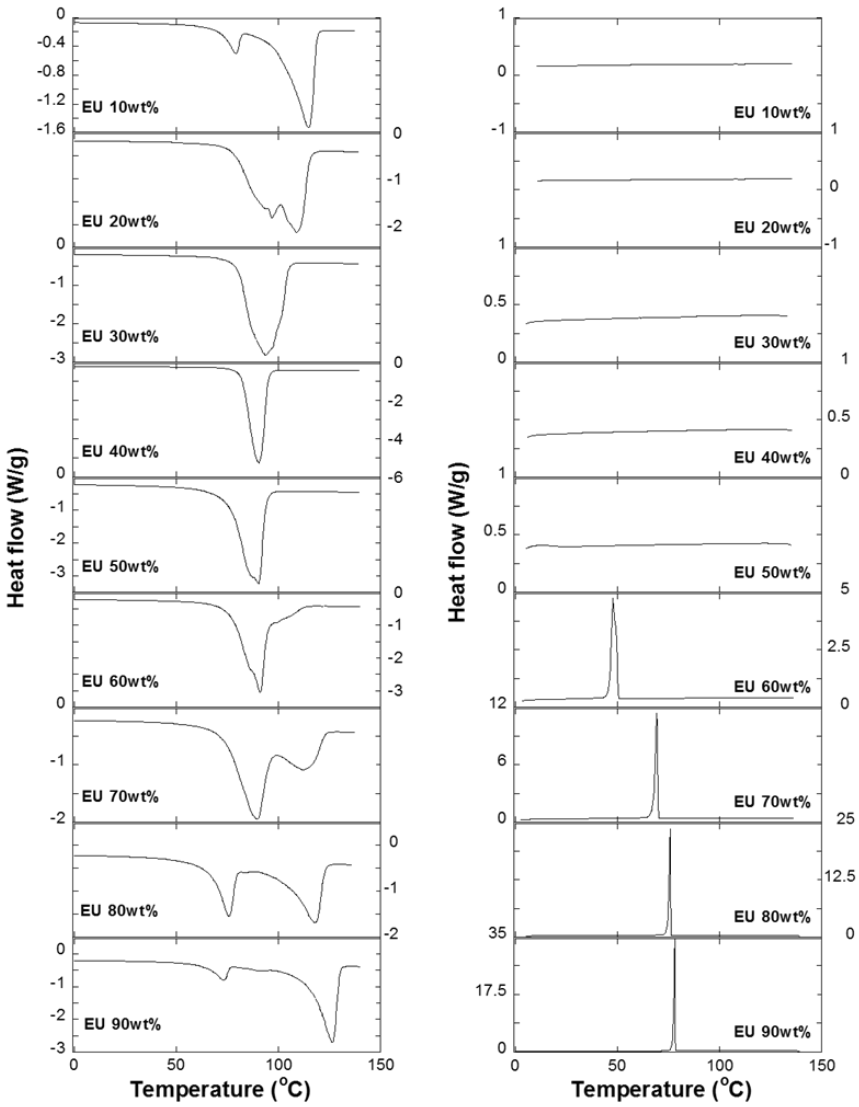

Figure 1. Melting (left) and crystallization (right) curves for erythritol-urea blends (EU) with different weight fractions of urea as given in the panels.

In case of melting, for both systems, both lower and higher fractions of urea result in two melting peaks whereas at intermediate fractions, there is one single peak. The latter suggests a eutectic composition, which in case of erythritol is around 40 wt% urea and in case of mannitol in the region of 50-60 wt% urea. However, as can be observed from the right panels, not all compositions crystallize. For the erythritol-urea (EU) system, there is no crystallization at lower fractions of urea. In this case, there is a need for around 60 wt% urea to initiate crystallization. For the mannitol-urea (MU) system on the other hand, there is only a lack of crystallization at an intermediate fraction, i.e. at 40wt%, of urea. In addition, for some of the mannitol-urea compositions there are two crystallization peaks. The thermal scenario for the erythritol-urea (EU) and mannitol-urea (MU) systems is thus rather complex.

To further investigate and visualize this complexity a phase diagram, based on the peak temperatures in figures 1 and 2, was constructed. The result is shown in figure 3.

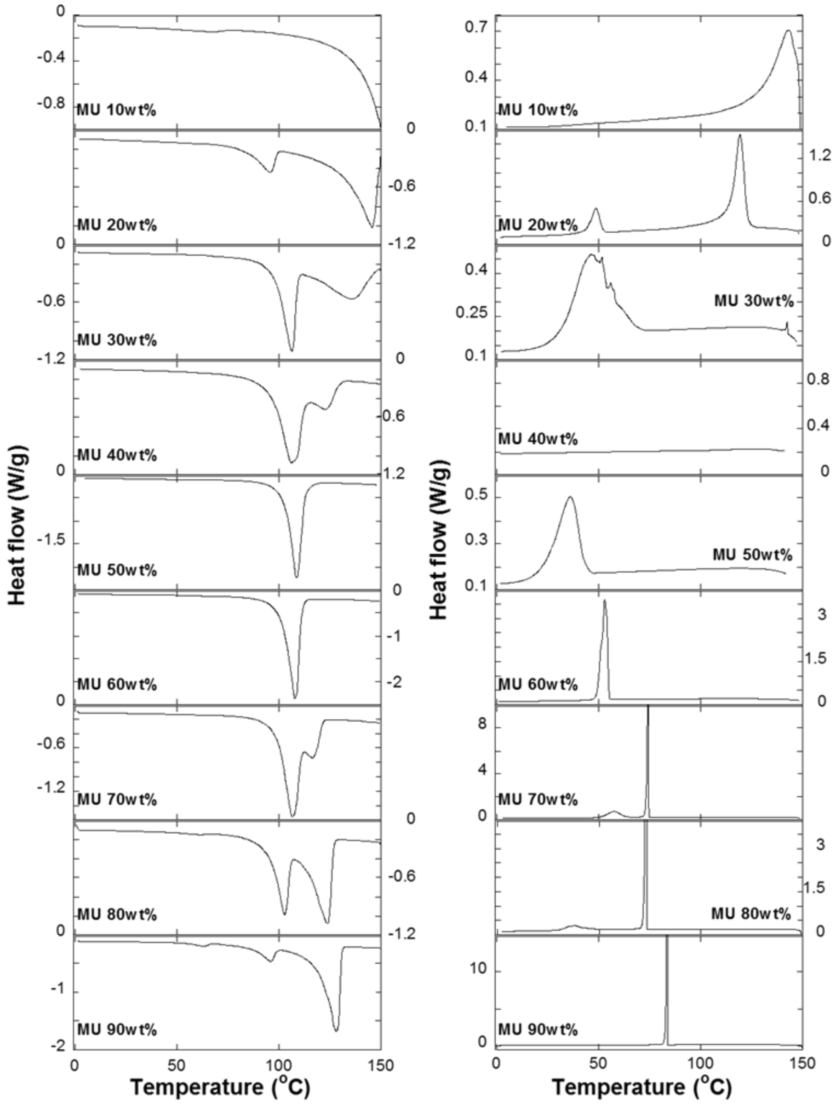

Figure 2. Melting (left) and crystallization (right) of mannitol with urea (MU) of different weight fractions as given in the panels.

As obvious from figures 1-3, the addition of urea results in rather large changes of thermally induced event of both the EU and MU systems. Since melting and crystallization events reflect the crystal structure of a system, the results therefore also imply that the structure of the systems, for most of the compositions, is not homogenous.

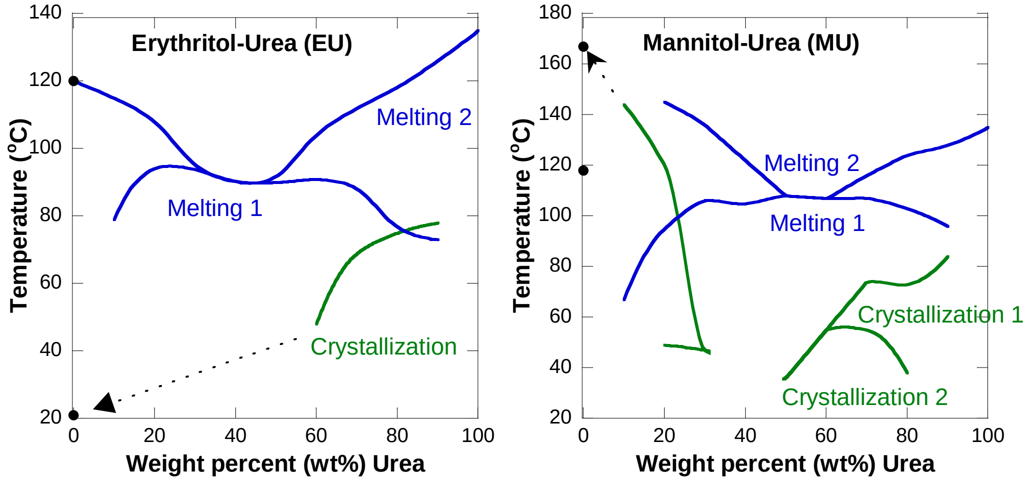

Figure 3. Phase diagrams obtained for erythritol and mannitol with urea of different weight fractions. Note here that the supercooling is smallest in the MU-system of around 20 and 70 wt% urea and that no crystallization was obtained for the EU-system of lower fractions of urea or for the MU-system with around 40 wt% of urea.

Rather the structure is composed of different types of crystal structures, which each giving rise to different melting and crystallization temperatures. Some of the structures are more stable than others. The more stable the crystal structure is, the larger is the supercooling.

4. Conclusions and future outlook

Obviously it is possible to change the phase transition temperatures of the sugar alcohols erythritol and mannitol by use of urea. Dependent on the composition, it is also possible to reduce the supercooling of the systems. For most of the compositions there are two melting peaks, which each should reflect a specific type of crystal structure. For each system it is also possible to obtain a eutectic composition, i.e. a composition with one single structure. Future plans involve investigations on larger samples of the same compositions by the T-history method. In addition, structural investigations should probably give valuable information about the differences between the different compositions.

5. Acknowledgement

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6. References

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