

Research on xylitol crystallization by shearing and seeding for its use as a phase change material

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Abstract. As thermal energy storage is becoming more important, new materials are being studied. Sugar-alcohols (SA) are very promising as phase change materials (PCM) because they are non-toxic, affordable and their latent heat is high. However, undercooling and low crystallization rates are some of the problems present in these materials. The SA studied in this work is xylitol, and using a microscope connected to a transparent counter-rotating shear cell, the effect of secondary nucleation is studied, as well as the crystallization rate of xylitol and how undercooling affects it. From the results, it is deduced that a proper seed preparation and handling is needed. The crystal structure is also studied, using XRPD diffractograms and differential scanning calorimetry.

1. Introduction

Due to the intermittency nature of energy sources and the not temporal coincidence between availability of this sources and demand of energy, the study of energy storage is needed. Thermal energy storage (TES) is one way to store energy and in this work latent heat TES is studied. The materials used are called phase change materials or PCMs. There are lots of materials used as PCM (molten salts, paraffins, etc.) but this study focuses on sugar-alcohols (SA), specifically in xylitol. SA, or polyols, are neither toxic, corrosive nor flammable, and they are nature abundant and usually cheap [1,2]. There are two main downsides for these materials; undercooling and low crystallization rates, which make polyols not suitable as PCMs. Previous works studied techniques to accelerate crystallization such as bubbling [3]. In this work, the effect of shearing in the crystallization process is studied.

The principal force involved in crystallization of xylitol is secondary nucleation. Secondary nucleation mechanisms involve three phases: Initial breeding, dendritic or needle breeding in the crystal surfaces, and attrition of these needles due to some mechanical forces [4,5]

2. Materials and methods

2.1. Materials

Xylitol (99% purity) purchased from Sigma Aldrich was used. Its formula is $C_5H_{12}O_5$ and its CAS number is 87-99-00. Regarding its physical properties, its density is 1.52 g/ml (in liquid state), its melting point is 94.3°C, and its latent heat is 239.3 J/g [1]. It is assumed that no moisture was adsorbed during sample preparation. Xylitol seeds had a radius between 315 and 400 μm . These seeds were obtained by sieving xylitol chunks as directly received from Sigma Aldrich.



2.2. Methods

2.2.1. Rheo-optical shear experiments. For these experiments, the counter-rotating shear cell in figure 1 was used. This shear cell was mounted on an optical microscope equipped with a CCD Camera, and the temperature was controlled using some heating elements and an oven, using 90°C as the selected temperature. The sample was loaded in three steps. Firstly, half of the previously molten xylitol was loaded in the cell. Secondly, three xylitol seeds were added and, finally, the other half of the molten xylitol was loaded. Once these steps were done, the gap was set at 1 mm and the shear was applied. Using the microscope, a seed was found and selected. The shear rate was then modified to observe its influence.

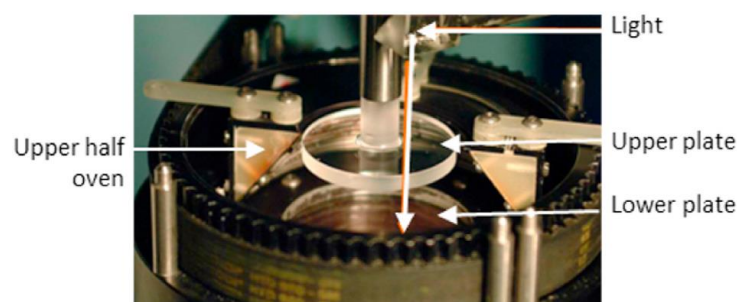


Figure 1. Counter-rotating shear cell, with transparent lower and upper plates.

2.2.2. Shear experiments. For these measurements, the rheometer used was a controlled stress rheometer from TA Instruments, an AR-G2 model. The geometry used was the parallel plate geometry, in which its diameter is 40 mm. The gap used was 600 μm , bigger than the seed size to avoid friction between the geometry and the seed. The procedure consists of loading half of the initial molten xylitol on the Peltier plate, adding a seed and then loading the rest of the molten xylitol. Measurements were done using three different shear rates and temperatures.

2.2.3. Polarized microscopy observations. Xylitol crystals were observed in both air and molten xylitol by cross polarisers (LeicaDM 4500P). Molten xylitol was placed in a slide located on a Linkam LTS 350 heating stage that controlled the temperature. Micrographs were taken periodically.

2.2.4. DSC measurements. A Netzsch 200 F3 Maia differential scanning calorimeter was used. The purpose of these measurements was studying changes in crystal structure of xylitol, before and after doing the shear experiments. The samples were heated at a rate of 0.5 K/min, and their weight was of approximately 10 mg.

2.2.5. X-Ray diffraction experiments. These tests were done with a D-Max Rigaku, Ru300 diffractometer, at 40kV and 80mA. The step size of 2θ of 0.03 was selected, going from 5 to 40°. These measurements were done to study the crystal structure of xylitol, and to complement the DSC results.

3. Results

3.1. Rheo-optical and shear experiments

3.1.1. Description of seeds. Seeds have an irregular form and can be an aggregated crystal chunk, as shown in figure 2. Also, some xylitol dust can be observed. These seeds were obtained sieving crystalized xylitol. Xylitol dust observed on the crystal surface can appear due to the preparation process

and handling of the sieved sample. As this dust is not holding on tightly to the surface of the crystal, it can act as a secondary nucleation site.

3.1.2. Description of seeds in molten supercooled xylitol. First, the seeds are placed in the molten xylitol. Then, one of the seeds is selected to be observed with the optical microscope. It is observed that in some of the experiments, seed size has increased due to the low shear caused by the work from the counter-rotating cell and the time it takes to find a seed. The crystal form of xylitol is orthorhombic, which can be observed when the crystal grows in the melt.

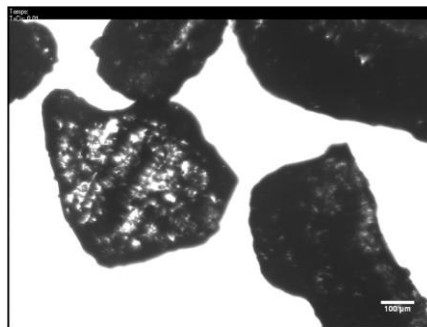


Figure 2. Xylitol seeds used in the experiments.

3.1.3. Effect of shear on seeds. Two different crystallization mechanisms can be found. At high shear rates, both agglomeration and deagglomeration of crystals is possible. Deagglomeration of xylitol clusters can be seen in figure 3. However, at low shear rates, deagglomeration was not observed. At shear rates higher than 20 s^{-1} , very small crystals were detected. Attrition of the seed can take place if small fragments erode the initial seed because of turbulence in the molten xylitol. There are two factors that influence deagglomeration of crystals: mechanical strength of the cluster and the breaking forces applied to it. Crystallization only starts when a seed is added to the molten xylitol. Crystal mass concentration, crystal mechanical properties, size and shape are important parameters when studying this system.

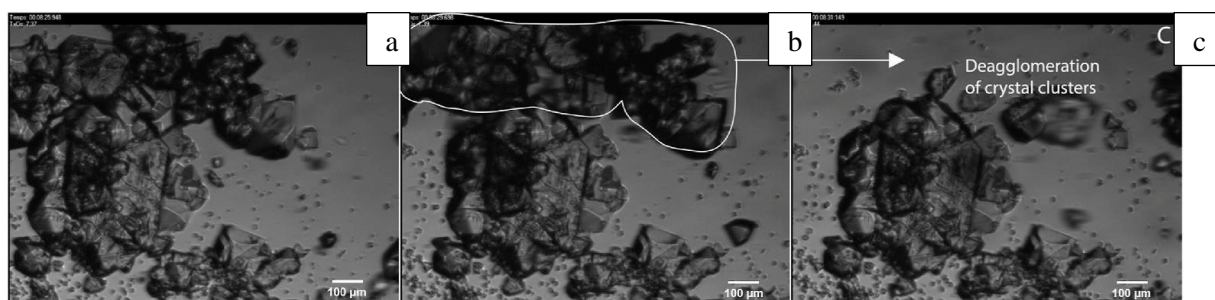


Figure 3. Dissagregation of a crystal cluster when shearing at 20 s^{-1} and 90°C . Time difference from a) 4s for b) and 6s for c).

3.1.4. Effect of shear in xylitol crystallization. Different measurements were done as defined in section 2.2.2. First, the loaded xylitol was molten on the Peltier plate and then the temperature was fixed on 90°C . After waiting for 20 minutes, a seed was added. Then, the other half of the molten xylitol was added. This part of the molten xylitol had been preheated in an oven at 90°C . Once all xylitol mass is added, the experiment started, measuring viscosity until the sample was totally crystallized. When the experiment ended, a new sample was prepared. The experiments were done at a shear rate of 5, 10 and

15 s⁻¹ and the temperatures selected were 70, 80 and 90°C. In both figures 4 and 5, three different regions can be observed. First, there is a region where viscosity does not change (Induction time); and then viscosity grows until the whole sample has been crystallized (Crystallization time). In some samples, a third region appears, where viscosity starts to stabilize again, showing a near constant viscosity, this zone probably exists due to the break-up of the network.

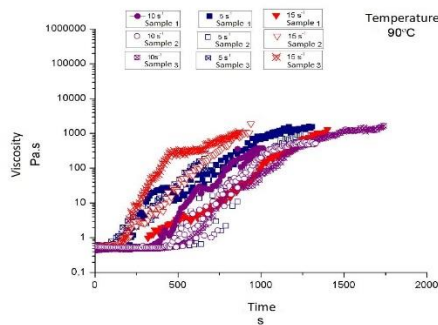


Figure 4. Viscosity evolution for different shear rates (5 s⁻¹, 10 s⁻¹, 15 s⁻¹) at constant temperature (90°C)

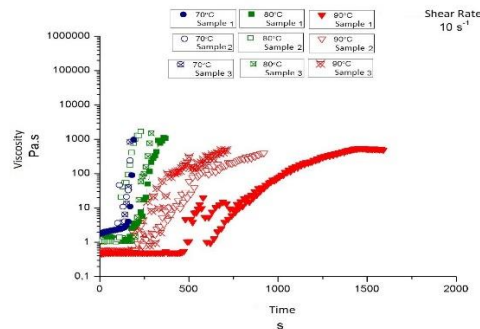


Figure 5. Viscosity evolution for different temperatures (70°C, 80°C, 90°C) at constant shear rate (10 s⁻¹)

3.2. DSC measurements

Melting temperature and latent heat of fresh and sheared xylitol were measured. (Table 1). There are not significant differences between each other, so it can be concluded that there are no changes in crystallinity between samples. The different enthalpy curves for each shear rate are shown in figure 6.

Table 1. Latent heat and melting temperature for fresh and sheared xylitol

Sample	Mass (mg)	Latent heat (kJ/kg)	Melting temperature (°C) (onset temperature)	Peak temperature (°C)
Fresh xylitol	16.78	241.2	92.8	94.7
Xylitol sheared at 5 s ⁻¹	14.48	233.6	92.7	94.4
Xylitol sheared at 10 s ⁻¹	14.27	236.3	92.8	94.5
Xylitol sheared at 15 s ⁻¹	11.27	238.2	92.5	94.1

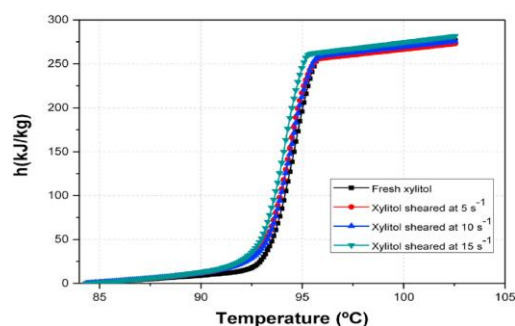


Figure 6. Enthalpy-temperature curve for different xylitol samples.

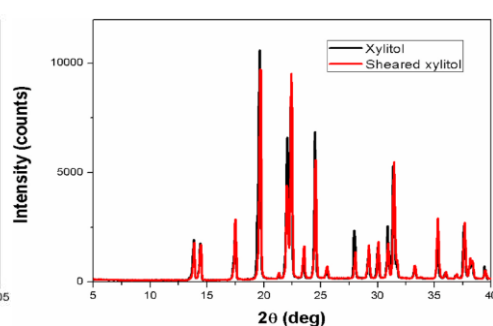


Figure 7. Diffractograms for bulk and sheared xylitol.

3.3. X-Ray diffraction experiments

Diffraction patterns of fresh xylitol and sheared xylitol were done. The diffraction patterns that appear in Fig 7. show that they are identical, as expected. In agreement with the DSC measurements, it can be concluded that there are not changes in crystallinity between fresh and sheared xylitol.

4. Conclusions

Coupling seeding with shearing has been proposed as a method of triggering and accelerating the crystallization in xylitol, so it can be promising as a PCM in short-term TES application. Rheo-optics techniques were used for studying the crystal before and during shearing, showing that xylitol dust could be a nucleation site and that attrition of the seed can occur due to this dust. Even though this phenomenon works better at higher rates, this can cause deagglomeration of crystal clusters formed.

The experiments performed with the rheometer shows that shear does accelerate crystallization rate, even though experiments do not have clear behavior patterns. Further research should be carried to develop similar seeds to ensure repeatability. DSC and XRPD measurements have proven that shearing xylitol does not change its crystal structure.

Acknowledgments

This work was developed in the frame of the research project ENE2017-87711-R, partially funded by the Spanish Government (Energy Program), the Government of Aragon (Ref: T55-17R), Spain, and the EU Social Fund (FEDER Program 2014-2020 "Building Europe from Aragon"). This research was partially carried out by Mónica Delgado during a research stay at the Centre de Mise en Forme des Matériaux (CEMEF)-CNRS-Mines Paris Tech, funded by a grant from Programa CAI-IbercajaEstancias de Investigación. *Authors would like to acknowledge the use of Servicio General de Apoyo a la Investigación-SAI, Universidad de Zaragoza*

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