Xylitol used as phase change material: Nucleation mechanisms of the supercooling rupture by stirring

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Abstract

With a very high energy density, Xylitol is a promising phase change material for low temperature heat storage (< 100°C). However, it has a high and persistent supercooling, which inhibits the latent heat restitution during thermal discharges. Bubbling in supercooled Xylitol has already been identified as an efficient crystallization triggering technique. This paper provides a detailed analysis of the nucleation mechanisms involved. A first conclusion is that primary nucleation has shown to be impossible to activate by stirring or shearing in reasonable timescales. This leads to a description of the crystallization based on secondary nucleation. A particular attention was paid to unintentional seeding, which showed to be likely the starting point of most of the Xylitol crystallizations observed in literature. Coupling seeding and bubbling was then identified as an improvement of the nucleation triggering technique. Adding a seeding step to the discharge protocol indeed leads to faster and reproducible crystallizations. In a second part, a parametric study, conducted for a mechanical and a bubbling agitation, showed that secondary nucleation in Xylitol is a thermally activated mechanism. Therefore, surface nucleation was proposed as the main source of secondary nuclei. Finally, a first model for the surface nucleation in supercooled Xylitol, emphasizing on the influence of Xylitol viscosity, was proposed.

Keywords:

- Phase change materials
- Sugar alcohols
- Crystallization
- Surface secondary nucleation
- Seeding

1 Introduction

Thermal energy storage systems are integrated in district heating networks to deal with the gap between heat production and demand. They facilitate the integration of intermittent energy sources such as renewable energies or wasted heat. Latent Heat Thermal Energy Storage (LHTES) systems are particularly suitable for decentralized applications, directly in the building substations of the network [1], [2]. Such applications indeed require compact solutions, which matches with high energy densities of LHTES systems. In addition to a high energy density, the Phase Change Material (PCM) used in a decentralized storage device must have a melting temperature below 100°C, the maximum temperature provided in building substations. The ideal PCM must also be cheap, non-toxic, non-flammable and environmentally friendly.

Among the different groups of possible materials studied in the literature [3], [4], Sugar Alcohols (SAs) were identified as promising candidates by Palomo del Barrio et al. [5]. They possess more than twice the energy density of paraffins wax, currently the most common PCM for such applications. They are used as sweeteners in the agribusiness industry, so they are edible and cheap. The main drawback of SAs is their high and persistent supercooling, which inhibits the crystallization of the PCM and the latent heat restitution. Shao et al. [6] studied several SAs and eutectics with melting temperature below 100°C and showed that they were indeed unable to recrystallize solely by cooling. This problem also applies to Xylitol, the SA studied in this work.

Xylitol is a 5-carbon polyol produced from D-xylose. It has a particularly high potential as PCM with a melting temperature of 93°C [7], a latent heat of 240 J/g [7] and a total energy density close to 120 kWh.m⁻³, when considering a temperature range from 30°C to 100°C [8]. However, Xylitol has a low primary nucleation rate [9], making it uncrystallizable by cooling [6]. Moreover, because of its high viscosity, Xylitol has a low crystal growth rate, with a maximum of approximately 3.5 μ m/s at 62°C [10], which drastically reduces the latent heat restitution speed. A recent review article by Safari et al. [11] provides a presentation of the influence of the PCM nucleation and crystal growth rates on the thermal discharge in LHTES systems. To initiate the latent heat restitution of Xylitol, a crystallization triggering technique that creates many nuclei in the supercooled PCM is required. This way, the total growing surface of the nuclei offsets the low Xylitol crystal growth rate and reduces the overall discharging time.

Nucleation, the formation of new crystals called nuclei, can occur via primary or secondary mechanisms. Nuclei formed by primary nucleation come from molecules of the liquid phase, which reorganize themselves into a crystalline structure. Therefore, high supercooling is the result of a low primary nucleation rate. For example, for highly viscous melts, the low diffusivity of the molecules in the liquid phase prevents them from reorganizing and can lead to a persistent supercooled metastable state. Another difference is made between homogeneous and heterogeneous primary nucleation. The former occurs in the bulk of the melt whereas the latter uses foreign particles or container surfaces to facilitate the formation of nuclei by reducing the energy needed for their formation.

On the other hand, secondary nucleation uses pre-existing crystals of the species of interest as a source of new nuclei in stirred melts. This secondary nucleation can follow primary nucleation or be induced by the addition of seed crystals. It involves different mechanisms [12], [13], including:

- Initial breeding; crystalline dust swept off a newly introduced seed crystal. The number of fine particles on a seed crystal surface is finite and, therefore, initial breeding is only a limited source of nuclei.
- Attrition, or collision breeding; a complex mechanical process resulting from collisions between crystals and parts of the vessel. The damaged parental crystals may be observed directly after the attrition event.
- Surface nucleation; an activated mechanism which might correspond to the detachment of weak outgrowths by the flow turbulences or the formation of nuclei in a layer adjacent to the crystalline growing surface. Like primary nucleation, it depends on the supersaturation but its metastable zone width is shorter, making it easier to activate. Surface nucleation is by far the most important source of secondary nuclei in industrial crystallizers, due to low agitation energy levels necessary compared to attrition.

All these secondary mechanisms require the initial presence of the crystalline phase, which means that secondary nucleation cannot be used to break the supercooled state but only allows to accelerate the crystallization by creating more nuclei. In industrial crystallizations, seeding is often used to initiate secondary nucleation at low supersaturation degree to control the quality of the newly formed nuclei.

Xylitol is often presented as an example of disappearing polymorph [14], [15] and a good understanding of this notion is crucial to discuss the nucleation mechanisms of Xylitol. Xylitol was first prepared in 1891 and was believed to exist only as a liquid until 1941, when a crystalline form was observed for the first time. This form had a melting temperature of 61°C. The current form, which melts at 93°C, appeared two years later and quickly replaced the first less stable polymorph. Nowadays, the polymorph melting at 61°C has completely disappeared and any attempt to crystallize it leads to the more stable form. This first metastable polymorphic from is thus called a "disappearing polymorph". Xylitol globally remained liquid for 50 years because of its very low primary nucleation rate. Then, the less stable polymorphic form appeared first because the energy barrier to overcome for its formation was lower than the one for the formation of the current form. This is known as Ostwald's rule of stages [16]. According to this historical testimony, triggering Xylitol primary nucleation within reasonable timescales for a LHTES application seems particularly difficult. However, as Dunitz and Berstein [14] explained, it is certainly possible to trigger primary nucleation of any Xylitol polymorph again, but it requires finding the right experimental conditions and waiting long enough.

Among the different nucleation triggering techniques in literature [17], several have already been tested on supercooled Xylitol. Seppäla et al. [18] tried to increase the growth rate of Xylitol using additives to speed up the latent heat restitution after seeding. For example, the addition of a 5% ethanol concentration (mass ratio) led to crystallization rates 10 times higher than the ones in pure Xylitol. However, this increase is too small for an urban heating network storage application. Moreover, the reason of this increase is not yet fully understood: Hartwig et al. [19] showed that the addition of ethanol rather decreased Xylitol growth rate for crystallizations in solution. Godin et al. [20] showed that local cooling fails to initiate Xylitol crystallization and that seeding and high-power ultrasounds have a very localized effect and cannot create enough nuclei. Finally, the authors proposed bubbling agitation as a promising option to trigger the formation of many nuclei in the entire stirred volume of supercooled PCM. Their hypothesis is that primary nucleation occurs at the surface of small bubbles generated by the agitation. Duquesne et al. [21] showed that mixing mechanically a 400 mL Xylitol sample at 45°C initiates a massive nucleation in only a few seconds. More recently, Coccia et al. [22] triggered Xylitol nucleation in a portable solar box cooker by mechanically stirring the PCM sample. Delgado et al. [23] proposed a combined technique of seeding and shearing to trigger and accelerate Xylitol crystallization, using secondary nucleation mechanisms to increase the total crystal growing surface.

If stirring or bubbling seems to be a promising technique to trigger Xylitol crystallization, the nucleation mechanisms involved are still not well understood. More generally, if it is commonly accepted that stirring in a supercooled PCM allows to trigger its crystallization, Mullin [15] emphasized on the complexity of this method and the difficulty of differentiating nuclei formed by primary and secondary nucleation. Therefore, the present work studies the feasibility of triggering Xylitol crystallization by stirring or bubbling for a short term LHTES application and discusses the nucleation mechanisms involved. To start with, the feasibility of triggering primary nucleation in supercooled Xylitol by shearing or stirring was experimentally studied. Facing an impossibility to trigger primary nucleation in reasonable timescales, secondary nucleation was proposed as the main source of nuclei in stirred supercooled Xylitol samples and seeding was proposed as an efficient way to control and accelerate the crystallization. A parametric study of the secondary nucleation induction time in supercooled Xylitol was also performed, showing that most of the newly formed nuclei probably come from surface nucleation. Finally, first models of the surface secondary nucleation were proposed, with a view to provide models of Xylitol's crystallization kinetics for the design of future real LHTES devices.

2 Understanding the nucleation mechanisms in stirred Xylitol

2.1 Xylitol characterization

Xylitol was purchased from Danisco (purity 98.5%). According to the supplier, the Xylitol powder particles have a mean diameter of 180 μ m and are composed of many small aggregates. In this first section, thermodynamic properties of Xylitol were measured and compared to values of literature. The chemical stability of the Xylitol sample used in this work was also verified.

The melting temperature and the fusion enthalpy of the purchased Xylitol sample were measured using a micro scanning calorimeter from Setaram. The measured thermal capacity is presented in red in Fig. 1, and was obtained using 326 mg of Xylitol and a heating rate of 0.1°C/min. The obtained melting temperature of 93.1°C, corresponding to the onset temperature [24], is close to the value obtained by Diarce et al. [7]. The same observation can be made for the measured fusion enthalpy and specific heat capacities.



Fig. 1. DSC thermograms of the pure original Xylitol sample (326 mg) and the degraded sample (1500 hours at 100°C) with a heating/cooling rate of 0.1°C/min. $T_m = 93.1$ °C; $\Delta H_m = 238 \text{ J/g}$; $c_{p-liq} = 2.7 \text{ J/g/K}$; $c_{p-sol} = 1.8 \text{ J/g/K}$.

In Fig. 1, the cooling ramp following the first melting is also represented in blue to illustrate the high and persistent Xylitol supercooling. Indeed, the melted Xylitol sample cooled down to 60°C without crystallizing, due to the very low Xylitol primary nucleation rate. This DSC curve replicates previous results of Shao et al. [6], which showed that Xylitol is uncrystallizable by solely cooling.

Another DSC thermogram was also conducted at the end of the experimental campaign to check the Xylitol sample's chemical stability. The sample passed around 1500 hours at 100°C under a flux of N₂. The DSC thermogram of the degraded sample was realized using the same heating rate and is represented in Fig. 1 in yellow. No degradation of the fusion enthalpy nor the melting temperature was observed, indicating a good thermal and cycling stability, as Biçer et al. [25] and Zhang [26] already stated. However, the Xylitol sample turned surprisingly yellow, even if Xylitol is not supposed to undergo Maillard reaction (browning reaction) [27]. This coloration may be explained by the oxidation of the impurities in the sample or a complex caramelization reaction involving xylose. Thanks to the DSC results, Xylitol was considered chemically stable in this work. However, future works may focus on providing a detailed analysis of Xylitol chemical and thermal stability.

2.2 Forcing primary nucleation by shearing

The feasibility of triggering Xylitol primary nucleation by shearing or stirring in a supercooled sample was first investigated. In a stirred PCM, nucleation may occur via primary or secondary nucleation. Then, it was crucial to work on isolated samples, protected from unintentional seeding. Indeed, a single dust of crystallized Xylitol settling at the free surface of the supercooled sample may trigger secondary nucleation and completely interfere with the test. Two triggering methods were explored: by shearing in a rheometer or by stirring in a beaker.

2.2.1 Rheometer trials - Methods

A plate-plate rheometer MCR300 was used to investigate the feasibility of triggering the crystallization of a 2 mL supercooled Xylitol sample by shearing. The upper plate had a diameter of 50 mm and the plate-plate distance was fixed at 1 mm. Different shear rates were then applied between 1 s⁻¹ and 100 s⁻¹. The temperature of the Xylitol sample was controlled by a Peltier element integrated in the lower plate. The Xylitol viscosity was measured to detect the beginning of crystallization.

The Xylitol sample was first heated for three hours at 105°C to ensure a complete fusion. Then, the upper plate was placed over the sample and a tap was used to limit thermal losses and to protect the sample from unintentional seeding. Moreover, the rheometer was placed in a room where crystalline Xylitol had not been handled before. The experimental protocol started with a linear cooling ramp from 105°C to 50°C in one hour. The sample was sheared at a constant shear rate as soon as the sample temperature started decreasing. At the end of the cooling ramp, the sample was maintained at 50°C under constant shear rate. Nucleation was supposed to be detected by a sudden increase in viscosity.

2.2.2 Rheometer trials - Results

Fig. 2 presents a typical result using the rheometer, with the sample temperature and the measured viscosity. For the first hour, Xylitol viscosity increased as the sample temperature decreased, following Shao et al.'s viscosity curves [28].Only the first three hours were represented in Fig. 2, however, the Xylitol sample never crystallized even after shearing it 48 hours at 50°C. Other shear rates (between 1 s⁻¹ and 100 s⁻¹) and other temperatures (between 30°C and 90°C) were also tested, unsuccessfully; the Xylitol sample never crystallized.



Fig. 2. Trial to initiate Xylitol crystallization by shearing in a rheometer PP50 under a constant shear rate of 50 s⁻¹ and a plate-plate distance of 1 mm. In red: the sample temperature. In blue: the measured sample viscosity.

It seems that shearing does not increase Xylitol primary nucleation rate enough to trigger its crystallization. However, the lack of nucleation sites and the small sample size could also have contributed to the difficulty in triggering primary nucleation.

In Fig. 2, it can also be observed that Xylitol viscosity seems to slowly decrease with time for a constant sample temperature and shear rate. The rheometer used in this work has no known drift in measurement, so this observation points towards a possible thixotropic behavior of the supercooled Xylitol sample. Shao et al. [28] showed that Xylitol is a non-Newtonian fluid for shear rates smaller than 1 s⁻¹ and a Newtonian fluid above, but they did not study the Xylitol thixotropy. A more detailed analysis of the rheological behavior of supercooled Xylitol would then be necessary to support this hypothesis. Therefore, it has not been discussed further in this work.

2.3 Initiating primary nucleation by stirring

2.3.1 Magnetic stirrer - Methods

In this section, attempts to trigger Xylitol crystallization by stirring are presented. A beaker filled with 20 mL of supercooled Xylitol and containing a magnetic stirrer is depicted in Fig. 3. The beaker was hermetically closed to avoid unintentional seeding and then placed in an oven at 105°C overnight to melt the entire sample. The next day, the beaker was placed on a magnetic agitation plate. The sample temperature was fixed using the plate's

electric heater. Various temperatures from 60°C to 90°C have been tested. At the end of each trial, a thermocouple was used to check the temperature of the PCM sample. The nucleation was detected visually.



Fig. 3. Triggering nucleation by stirring in Xylitol: a hermetically closed beaker filled with 20 mL of PCM and a magnetic stirrer. After two weeks of stirring without crystallization, a thermocouple was put in the PCM to check its temperature: 70°C.

2.3.2 Magnetic stirrer - Results

In the hermetically sealed beaker, no crystallization occurred even after two weeks of stirring at the different tested temperatures. Not a single nucleus appeared in the stirred volume V in a Δt of two weeks, which led to the following order of magnitude for the primary nucleation rate [29] (Eq. (1)):

$$J \ll \frac{1}{V \cdot \Delta t} = 10^{-8} s^{-1} cm^{-3} \tag{1}$$

Many possible nucleation sites were present inside the beaker (impurities, small bubbles, surface roughness, the magnetic stirrer, etc.). Compared to the rheometer trials, the presence of these nucleation sites, the increased sample volume and the higher vorticity of the stirring technique would normally help to force the crystallization, but they were not enough to induce a primary nucleation event in the Xylitol sample.

2.4 Discussion on Xylitol's nucleation mechanisms

2.4.1 The unfeasibility of triggering Xylitol primary nucleation

According to previous observations, it seems that it is impossible to trigger Xylitol primary nucleation by stirring or shearing in reasonable timescales for a short-term LHTES application. This observation is consistent with the timescales of the Xylitol industrial production history related by Dunitz and Berstein [14]. Even if a primary nucleation event occurred in a supercooled Xylitol sample, it is highly unlikely for it to be an intense mechanism capable of forming many nuclei, as needed in a LHTES system.

This conclusion is in contradiction with previous works from Duquesne et al. [21], who reported initiating a massive formation of nuclei within only a few seconds by stirring. However, another nucleation scenario, involving unintentional seeding and secondary nucleation, may explain the crystallizations they observed.

2.4.2 The importance of unintentional seeding

The major difference between the present experimental protocol and Duquesne et al.'s [21] experiments is the presence of the hermetical tap in our setup that prevents from unintentional seeding. In order to highlight the importance of sealing the beaker, similar experiments were repeated, but without tapping the sample. In this case, a massive formation of nuclei was observed after a few seconds of stirring, as Duquesne et al. [20] observed. The Fig. 4 represents a picture of the opened beaker after 2 minutes of agitation at 70°C. A massive formation of nuclei is observable, particularly nearby the magnetic stirrer, whereas the Xylitol sample was not intentionally seeded.



Fig. 4. A massive formation of nuclei in supercooled Xylitol in the opened beaker after 2 minutes of stirring at 70°C.

Without the hermetical tap, a crystalline Xylitol dust could have settled at the free surface of the sample and act as a parental crystal for secondary nucleation. Then, the presence of the crystalline phase in the stirred sample let secondary nucleation to happen. Delgado et al. [23] showed that even small shear rates in supercooled Xylitol can cause an massive formation of secondary nuclei. This unintentional seeding event can then completely interfere with the trials to initiate primary nucleation. Here, the apparition of this first parental crystal is an uncontrolled random event; which may explain the lack of reproducibility observed by Duquesne et al. [21] in their work.

To strengthen this hypothesis of an unintentional seeding, an opened beaker filled with supercooled Xylitol was simply placed in the lab. After a dozen hours, small crystals indeed appeared at the free surface, as shown in Fig. 5, whereas no nucleus appeared in the sealed stirred beaker after 2 weeks. The latency in the visual detection of the crystals can be explained by the small Xylitol growth rate and, in reality, these crystals could have appeared much earlier.



Fig. 5. Unintentional seeding at the free surface of a Xylitol sample kept in the lab atmosphere during 10 hours.

In his book *Crystallisation*, Mullin [15] dedicates pages 199 to 201 to this unintentional seeding problem: "unintentional seeding, also frequently encountered in both laboratory and industry, is an uncontrolled event which can often cause considerable frustration and trouble". Atmospheric dust frequently contains particles of crystalline products that have been handled in the laboratory. It is a well-known problem in industrial crystallization processes but authors working on supercooling rupture rarely consider this phenomenon. It is then crucial to prevent unintentional seeding events when studying the feasibility of triggering primary nucleation in supercooled PCMs, and particularly in paying attention to control the atmosphere nearby the studied samples

2.4.3 Triggering Xylitol crystallization coupling seeding and secondary nucleation

In the case of Xylitol, real LHTES systems will be exposed to unintentional seeding, probably because of incomplete fusions or crystalline dust contained in the atmosphere. Therefore, keeping in mind the timescales of such applications, Xylitol primary nucleation can be considered impossible to trigger, or at least negligible compared to unintentional seeding. All attempts to initiate Xylitol crystallization have to be analyzed in this light. Crystallizations observed by Coccia et al. [22] or by Duquesne et al. [21] were likely initiated by an uncontrolled self-seeding event followed by secondary nucleation.

Intentionally seeding then seems to be a relevant strategy to control and speed up the crystallization of supercooled Xylitol. Nevertheless, seeding still has to be coupled with stirring to create many secondary nuclei in the entire volume of PCM to offset the low crystal growth rate. Delgado et al. [22] already reported that coupling seeding and shearing might be an efficient solution to trigger and accelerate Xylitol crystallization. From few first

parental crystals, the high secondary nucleation rate allows to create many other nuclei and to increase the total growing surface.

In their work, Delgado et al. [22] emphasized on initial breeding and disaggregation mechanisms. The crystalline Xylitol powder they incorporated in their sample was formed of many small aggregates that shearing might break and disperse. However, the beaker in Fig. 3 underwent a massive formation of secondary nuclei without seeding it with aggregates. In that case, initial breeding cannot be a sustainable source of secondary nuclei and other mechanisms might be involved, such as attrition or surface secondary nucleation.

Coupling seeding and stirring seems to be a very promising technique to trigger Xylitol crystallization, but the mechanisms behind the secondary nucleation are not clearly identified. Therefore, the present work focused on proving the interest of this technique and identifying the secondary nucleation mechanisms involved in order to model the secondary nucleation rate.

3 Thermal discharges triggering crystallization by seeding and stirring

Coupling seeding and stirring was identified as a promising technique to trigger Xylitol crystallization in previous section. Therefore, this section studies the advantages brought by adding a seeding step to the discharge protocol of LHTES systems using Xylitol as PCM and a stirring device. Two stirring techniques were tested: bubbling at the bottom of the crystallizer and mechanically stirring the PCM with a propeller. For both types of agitation, thermal discharges with and without adding a seeding step to the experimental protocol were compared.

3.1 Experimental set up

3.1.1 Bubbling metallic crystallizer

The first crystallizer, shown in Fig. 6, was a double-walled metallic cylindrical crystallizer filled with 400 mL of the same Xylitol sample as previously studied (Danisco, purity 98.5%).



Fig. 6. Side and top views of the bubbling metallic double-walled crystallizer filled with 400 mL of supercooled Xylitol. 9 thermocouples are fixed on a rod at different positions. The thermocouples are located at three different heights and three positions; Exterior (E), Interior (I) and Rotational (R).

A needle injecting N_2 at the bottom of the vessel was used to agitate the liquid. A flow sensor was used to fix the gas flow at 1 L/min. The needle was slightly inclined (around a few degrees) to ensure a preferential path for bubble formation and the most reproducible agitation possible. The use of N_2 prevents any potential chemical reactions with air, such as those studied by Solé et al. [30] for other SAs. As stated in section 2.1, no significant degradation of the Xylitol sample was observed during the experimental campaign.

To lower the risks of unintentional seeding, a tap was placed at the top of the crystallizer. A small opening was made in the tap to seed the crystallizer.

The double-walled vessel was connected to a thermal bath using silicone oil (SilOil M40) as heat transfer fluid. The oil flow in the double wall was fixed at 85 kg/h. Two thermocouples were used to measure the inlet and outlet temperatures of the thermal oil. Nine other thermocouples (T-type 1 mm) were immersed in the PCM sample at different positions to check the thermal homogeneity of the stirred volume of Xylitol. Fig. 6 indicates the positions of these nine thermocouples; the thermocouple placed at the height '2' at the exterior position is referred to as the thermocouple 'E2'.

The Xylitol sample was considered perfectly homogeneous and the mean value of these nine thermocouples was used to represent the temperature of the sample. The start of latent heat restitution was detected by an increase in the PCM temperature. The entire experimental bench was thermally insulated.

3.1.2 Mechanical agitation in a glass crystallizer

A second double-walled crystallizer was also set up to study the effect of a mechanical agitation (Fig. 7). A propeller (Heidolph PR32 3 blades + ring, diameter 45 mm) compatible with the high viscosity of supercooled Xylitol was used to agitate the PCM sample at a constant rotational speed, fixed at 150 rpm by a motor Heidolph RZR 2041. The glass double-wall allows to follow visually the crystallization. This second crystallizer was built to check if the observations made with the bubbling crystallizer were still valuable for another stirring device. However, the multiple differences between both crystallizers (dimensions, PCM volume, cooling method, etc.) prevent a detailed comparison of their performances.



Fig. 7. Picture and diagram of the glass double-walled crystallizer mechanically stirred by a propeller and filled with 300 mL of supercooled Xylitol.

A tap was placed at the top of the crystallizer to avoid unintentional seeding. The vessel was filled with 300 mL of Xylitol and a T-type thermocouple was used to measure the temperature of the PCM. The double wall was connected to a thermal bath using the same silicone oil as in the previous crystallizer and a constant oil flow.

3.1.3 Discharge protocol

The experimental protocol presented in this section intends to replicate thermal discharges of a real LHTES system. In all the tests performed, Xylitol was initially melted at 105°C overnight to ensure a complete fusion. Then, the PCM sample was cooled down to 70°C and continuously stirred (by bubbling or by the propeller). The measured sample temperature was used to detect the start of crystallization by an increase in the PCM temperature. Measurement stopped few minutes after the supercooling rupture or after 160 minutes if no increase in the PCM temperature was observed.

For each crystallizer, two different experimental protocols were conducted, with or without adding a seeding step to the protocol. The cooling and stirring conditions were fixed. For tests integrating a seeding step, 20 mg of the crystalline Xylitol powder were introduced to the crystallizer when the PCM temperature went below 90°C. The seeds were simply settled at the free surface of the stirred PCM by the trap in the tap. The introduced crystalline particles were unable to melt since the temperature of the PCM was already below the Xylitol melting temperature (93°C). However, they should not be able to initiate the latent heat restitution by simple growth; the creation of many nuclei is still necessary to offset the low crystal growth rate of Xylitol and to obtain a sufficiently intense crystallization

Table 1 summarizes the experimental protocol of the thermal discharges for both crystallizers.

Table 1

Experimental protocol of the thermal discharges conducted in both crystallizers

	PCM volume	Crystallizer diameter	Thermal bath temperatures	Agitation
Bubbling INOX	400 mL	6.5 cm	105°C to 70°C	By bubbling: 1 L/min

crystallizer				Needle diameter: 1 mm
Glass crystallizer	300 mL	8.5 cm	105°C to 70°C	Propeller: 150 rpm Propeller diameter: 4.5 cm

For the samples that crystallized, the PCM temperature was also used to calculate the induction time between the beginning of the metastable state, when the PCM temperature passed bellow 93°C, and the moment when the latent heat restitution was detected. The induction time was used to compare the reproducibility and the performances of the different thermal discharges.

3.2 Results

3.2.1 Monitoring the temperature of Xylitol

The Xylitol temperature of several discharges is presented in Fig. 8 for mechanical agitation and Fig. 9 for bubbling agitation, using the mean value of the nine thermocouples. In Fig. 8, five discharges without adding a seeding step and three including it are plotted. For each trial, its corresponding induction time is also represented. A cross symbolizes the seeding event of the three concerned discharges.



Fig. 8.Xylitol supercooling ruptures, with or without a seeding step, for a mechanical agitation. Propeller rotational speed: 150 rpm; temperature of the thermal bath: 70°C.



Fig. 9. Xylitol supercooling ruptures, with or without a seeding step, for a bubbling agitation. Gas flow: 1 L/min; temperature of the thermal bath: 70°C.

Three pictures of the glass crystallizer at different moments of a discharge without seeding are also represented in Fig. 8. The first picture shows the melted sample before starting the discharge. The second one was taken at the beginning of the latent heat restitution, when the sample temperature started to increase. Many nuclei can be observed in the crystallizer. The last picture was taken one minute later; the sample looks more like a solid phase.

For the five trials without seeding in the mechanically stirred crystallizer, the induction time varied from a few minutes to several hours despite similar experimental conditions. On the contrary, the induction time for the three trials integrating a seeding step were equal and shorter than the ones measured without seeding.

The same observations can be made for the bubbling crystallizer. In Fig. 9, six discharges without the seeding step and three with it are presented. Four samples among the six without seeding did not crystallize after two hours of bubbling in the supercooled melt. If the other two did crystallize, their respective induction times are different. Therefore, adding a seeding step to the discharge protocol induced again shorter and reproducible induction times.

Table 2 summarizes the different measured induction times for both crystallizers.

Table 2

Measured induction times (in minutes) for both crystallizers, with and without seeding.

Induction time (min)	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6
Bubbling agitation	23	30	>150	>150	>150	>150
Bubbling + seeding	12	13	13			
Mechanical agitation	19	29	44	92	>150	
Mechanical agitation + seeding	10	11	11			

3.2.2 A lack of reproducibility without seeding

Based on the induction times presented in Table 2, triggering Xylitol crystallization by stirring without intentionally seeding the crystallizer may be possible but this technique is clearly not reproducible. A random unintentional

seeding event likely initiated these crystallizations resulting in such unreproducible induction times. Indeed, as showed above, primary nucleation in opened crystallizers is negligible compared to the risks of unintentional seeding. Then, the massive formation of nuclei observed in the second picture of Fig. 8 likely came from secondary nucleation.

Other thermal discharges were realized increasing the bubbling flow to 3 L/min and the rotational speed to 300 rpm. These experimental conditions were very close to the ones used by Duquesne et al. [21], However, even for these higher agitation intensities, the induction times obtained without seeding remained unreproducible. Fewer experiments without seeding led to crystallization in the bubbling crystallizer. The nitrogen flow could have contributed to isolate the main sample from crystalline dust of the atmosphere, reducing the risks of unintentional seeding. However, this protection was not perfect since two trials among the six tests performed without seeding did crystallize.

3.2.3 Controlling Xylitol crystallization by seeding

By adding a seeding step to the discharge protocol, the induction time was reduced and became reproducible for both crystallizers. In these conditions, secondary nucleation started as soon as the seeds were introduced and did no longer depend on an uncontrolled self-seeding event. Since the induction times obtained by seeding were reproducible, secondary nucleation in Xylitol seems to be an intense mechanism, as Delgado et al. [23] previously observed.

However, the latent heat restitution did not start immediately after the seeding event. As explained earlier, the seeds growth alone cannot induce the observed rapid crystallization and a massive formation of nuclei is necessary to offset the low crystal growth rate of Xylitol. Then, these new formed nuclei have to grow enough to induce an increase in the sample temperature. The latency between the seeding event and the latent heat restitution would thus be the real secondary nucleation induction time, representing two mechanisms, nucleation and growth [29].

For an application in a real LHTES system, bubbling would be a less intrusive stirring method than mechanical agitation. Then, coupling seeding and bubbling appears to be a very promising way to trigger Xylitol crystallization. However, for a real system application, optimizing the seeding strategy and the stirring conditions would be necessary to reduce the induction time as much as possible, because it results in a delay in the latent heat restitution and a variation in the restituted temperatures. Moreover, in order to design a future LHTES device using this triggering technique, a better understanding of the secondary mechanisms involved is necessary.

4 Parametric study on the secondary nucleation induction time

In this section, a parametric study of the secondary nucleation in supercooled Xylitol was realized with the two crystallizers of previous section. The goal of this study is to measure the induction time between the seeding event and the start of the latent heat restitution for different temperatures and stirring intensities. This induction time is particularly interesting because it depends on the secondary nucleation rate and will be useful to discuss the crystallization kinetics in stirred supercooled Xylitol.

4.1 Experimental setting

For both crystallizers, the Xylitol sample was completely melted overnight at 105°C. Then, the sample was cooled down to the chosen temperature. Stirring during the cooling ramp allowed to speed up the cooling step and to ensure a good homogeneity of the Xylitol sample. The crystallizer was seeded with 20 mg of Xylitol powder when the temperature of the PCM passed below the target temperature plus 1°C. This way, secondary nucleation took place at a rather constant temperature in the PCM and the cooling step was shortened as much as possible to avoid unintentional seeding.

Fig. 10 presents a typical discharge in the bubbling crystallizer, following the previously described protocol. For this trial, the thermal bath temperature was fixed at 75°C and the bubbling flow at 1 L/min. Temperatures from the nine thermocouples placed inside the PCM are plotted, using the same nomenclature as in the previous section. A cross represents the seeding event.



Fig. 10. Thermal discharge and measurement of the induction time in the bubbling crystallizer for a gas flow of 1 L/min and a thermal bath temperature of 75°C. T_m: Xylitol melting temperature.

In Fig. 10, three different zones are identifiable: the cooling ramp, the induction time and the crystallization. During the cooling ramp, the signals from the nine thermocouples in the stirred PCM were very close; the PCM sample was homogeneous. The induction time corresponds to the latency time between the seeding step and the start of latent heat restitution. After the crystallization started, the PCM temperature increased until 93°C, the Xylitol melting temperature. Since the thermal bath temperature was fixed at 75°C, the solidified PCM was cooled down to 75°C after the crystallization ended. The whole crystallization was represented for comprehension; only the induction time was studied in this work and complete crystallizations will be presented in a future publication.

For the bubbling crystallizer, the sample temperature Ts during the induction time was defined as the mean value of the 9 temperatures measured by the thermocouples between the seeding event and the start of crystallization. The induction time was detected by an increase in temperature of 0.05°C compared to the minimum temperature measured by the thermocouple. Nine induction times was thus calculated, one for each thermocouple. The induction time presented henceforth in this work corresponds to the mean value of these nine measured induction times.

For the glass crystallizer with mechanical agitation, only one thermocouple was placed in the PCM sample, which was considered perfectly homogeneous. T_S directly corresponds to the mean temperature during the induction time and the same sensitivity (0.05°C) was used to detect the start of latent heat restitution.

The parametric study on the induction time was conducted for two input parameters: the sample temperature Ts and a stirring parameter, the gas flow for bubbling agitation and the propeller rotational speed for mechanical agitation. In both crystallizers, the sample temperature varied from 55° C to 90° C. Three bubbling flows (0.11, 1 and 2 L/min) and three rotational speeds (70, 150 and 300 rpm) were also studied. The maximum studied agitation intensities, for 300 rpm and 2 L/min, correspond to the experimental limits of the crystallizers. For a bubbling flow close to 3 L/min for example, the melted Xylitol overflowed from the crystallizer. On the other hand, for 0.11 L/min, the homogenization quality of the stirred PCM started to decrease significantly. However, these stirring intensities are relatively close from the ones studied by Duquesne et al. [21] for bubbling agitation and by Delgado et al. [31].

4.1.1 Discussion on the experimental protocol and unintentional seeding risks

Compared to previous section, a N_2 injection was integrated at the top of the glass crystallizer to create a gas flow at the free surface to protect the main sample from an unintentional seeding event. The bubbling crystallizer was not modified.

For both crystallizers, only a few tests for low seeding temperatures (below 55° C) crystallized before reaching the desired temperature. Therefore, the study was limited to T_S higher than 55° C and the crystallizers were seeded as soon as possible, without waiting for a perfect thermal stabilization of the PCM. Before seeding, the absence of crystals in the stirred melt was always visually verified. Thus, very thin pre-existing crystalline particles were considered negligible compared to the introduced 20 mg of Xylitol.

4.1.2 Uncertainties in measurement

By choosing not to wait for thermal stabilization of the sample before seeding, the sample temperature, in reality, slowly decreased during the induction period. Problems of homogenization of the stirred melt can also influence the measurement. These questions were taken into account as sources of uncertainty in the measurement.

For the bubbling agitation, the total uncertainty in measurement ε_T of the sample temperature T_s was calculated using Eq. (2):

$$\varepsilon_T = \sqrt{\sigma_T^2 + \sigma_{au}^2 + \sigma_{tc}^2} \tag{2}$$

Where σ_T is the standard deviation of the temperatures measured by the nine thermocouples, $\sigma_{au} = 0.25^{\circ}C$ is the specific acquisition unit's uncertainty and $\sigma_{tc} = 0.5^{\circ}C$ is the specific uncertainty of the thermocouples. Twice the total standard deviation ε_T was used to get a 95% confidence level.

The same approach was adopted to estimate uncertainties on the measured induction time. For each bubbling flow, the standard deviation σ_{ind} of the nine induction times measured during the experiment was used to represent problems of homogenization in the formation of nuclei. Again, twice the standard deviation was used to get a 95% confidence level on the induction time.

Only one thermocouple was used in the mechanically stirred crystallizer, making impossible the estimation of the uncertainty due to the homogenization quality. Therefore, even if fluid mechanics of both crystallizers were completely different, the uncertainties calculated for the bubbling agitation were used to estimate those for the mechanical agitation. For the induction time, the relative error for a bubbling agitation of 1 L/min was rather constant between the different trials and the maximum error was then applied to the glass crystallizer, fixing $\sigma_{ind}/t_{ind} = 10\%$.

4.2 Results of the parametric study

4.2.1 The induction time

Over a hundred thermal discharges were conducted for both crystallizers. All the different measured induction times are presented in Fig. 11, using the sum of the different sources of uncertainties detailed in section 4.1.2 with a 95% confidence level.



Fig. 11. Parametric study on the secondary nucleation induction time for both crystallizers.

4.2.2 Influence of the agitation

Surprisingly, the induction time does not seem to depend on the agitation for both types of agitation. However, the high uncertainties may hide a second order influence of this parameter. Indeed, secondary nucleation mechanisms generally depend on the agitation intensity.

Induction times for mechanical agitation were generally lower than the ones obtained for bubbling agitation. A possible explanation would be that mechanical agitation involves more violent shocks than bubbling agitation, around the propeller in particular, resulting in more attrition breeding and a disaggregation of the injected seeds. However, it is difficult to go further in the comparison of both crystallizers because of their different dimensions

and PCM volumes. More generally, induction times are known to be difficult to extrapolate from a crystallizer to another and future works might focus on how to do so. What has to be retained from this work is that the measured trends of the induction time were similar for both stirring methods.

4.2.3 Influence of the sample temperature

For both crystallizers, the induction time decreased between 90 and 80°C and then remained nearly constant for lower temperatures. Close to a sample temperature of 70°C, it took only five minutes to initiate the latent heat restitution in the bubbling crystallizer and even less with a mechanical agitation. However, for bubbling agitation only, the induction time started to increase again for T_S lower than 60°C.

In the first zone, the induction time decreased with the supercooling degree, indicating a temperature dependent mechanism. However, induction time is the sum of the contributions, nucleation and growth, and crystal growth rate is known to increase with the supercooling degree. Therefore, an additional work would be necessary to distinguish both contributions.

For temperatures below 60°C, homogeneity problems started to be observed in the bubbling crystallizer, indicating a possible change in the bubbling structure. For such temperatures, Xylitol viscosity increases drastically when the temperature decreases, reaching 8 Pa.s at 60°C. Kulkarni et al. [32] showed that for viscous fluids, an increase in viscosity may result in an increase in the bubble size and affect the flow structure. As a result, the variation in the induction time in the bubbling crystallizer for temperatures below 60°C seems difficult to analyze, as bubbling was probably not able to stir efficiently the Xylitol sample for such high viscosities.

The secondary nucleation induction time in stirred Xylitol appeared to depend mainly on the temperature and not on the agitation intensity. In a real LHTES system using a seeding and stirring device to trigger the Xylitol crystallization, increasing the agitation intensity might not be a good way to reduce the induction time. Locally cooling the PCM, around the seeding point, may rather be a smarter strategy to initiate as fast as possible the latent heat restitution.

4.3 Study of the secondary nucleation rate

To identify which secondary nucleation mechanism is mainly responsible for the nuclei production in the stirred crystallizer, it is necessary to estimate the nucleation rate from the measured induction time. Modelling the nucleation rate would also help to predict the crystallization kinetics of the stirred Xylitol samples.

4.3.1 Formulation of the induction time

In this section, a formulation of the measured induction times was proposed to distinguish secondary nucleation from crystal growth. Secondary nucleation depends on the crystalline surface available for nucleation; the more nuclei are formed, the more the total crystalline surface increases, resulting in the creation of even more nuclei. Unfortunately, no model was found in literature to take into account this chain reaction. In this work, the secondary nucleation rate was then considered constant during the induction time, which allows to use primary nucleation equations to describe the phenomenon. The development of more complex models; designed specifically for the secondary nucleation in supercooled melts, will be the object of future works.

Based on Kolmogoroff's law for spherical nuclei, at a constant temperature and for primary nucleation, Kashchiev [29] gave in his chapter 29 the following equation to link the measured induction time to the nucleation rate (Eq. (3)):

$$t_{ind} = \left(\frac{\alpha_{crit}}{\frac{\pi}{3}G^3 J}\right)^{1/4} \tag{3}$$

Where J is the primary nucleation rate, G is the crystal growth rate and α_{crit} is the minimum transformed solid ratio for nucleation detection. α_{crit} is an experimental parameter and depends on the nucleation detection method. In this work, α_{crit} is linked to the increase in temperature used to detect the induction time.

To estimate α_{crit} , a thermal balance on the Xylitol sample during the induction time was realized. The Xylitol sample was considered adiabatic; the latent energy generated by the crystallization of a fraction α_{crit} of the supercooled liquid was only used to heat the Xylitol sample. Also, the solid heat capacity of Xylitol was neglected, since $\alpha_{crit} \ll 1$, resulting in Eq. (4):

$$\alpha_{crit} = \frac{\Delta T_d \cdot c_{p-liq}}{\Delta H_f} \sim 5.10^{-4} \tag{4}$$

Where ΔT_d corresponds to the 0.05°C sensitivity used to detect the induction time, c_{p-liq} is the Xylitol liquid heat capacity and ΔH_f is the Xylitol fusion enthalpy. This value indicates that only 5.10⁻²% of the supercooled Xylitol sample has already crystallized at the end of the induction time.

Crystal growth rate in the supercooled melt is known to strongly depend on the sample temperature but the influence of agitation seems to be really complex and not fully understood [33]. Many authors working on polymer crystallization assumed that G is a function of temperature only [34]. To our knowledge, not a single article in the literature has studied the influence of shearing or stirring on Xylitol crystal growth rate. Therefore, the same hypothesis, considering that Xylitol crystal growth rate is independent of agitation, was used in this work. Literature values [10] for Xylitol crystal growth rate in stagnant melts were thus applied to the studied crystallizers.

4.3.2 Parametric study on the secondary nucleation rate

Using equations (3) and (4) and hypothesis presented in section 4.3.1, secondary nucleation rate in the studied crystallizers can be calculated, using the measured induction time, as follows (Eq. (5)):

$$J_{sec} = \frac{\Delta T_d. c_{p-liq}}{\frac{\pi}{3} \Delta H_f G^3 t_{ind}^4}$$
(5)

Previous uncertainties in the measurement of the induction time were used to estimate the uncertainties for the secondary nucleation rate. Eq. (5) was used to calculate the uncertainty on J_{sec} knowing σ_{ind} , uncertainty in measurement for the induction time (Eq. (6)):

$$\sigma_J = \frac{4J_{sec}\sigma_{ind}}{t_{ind}} \tag{6}$$

Where twice σ_J represents the uncertainty on the secondary nucleation rate to get a 95% confidence level. Other sources of uncertainties may have been considered (for example uncertainties in the calculation of the crystal growth rate G, which depends on the sample temperature Ts) but σ_J is by far the most important source of uncertainty.

For the bubbling agitation and for the lowest gas flow (0.11 L/min), uncertainties of more than a hundred percent were obtained for the secondary nucleation rate, because of the lower homogenization quality. It was then decided to exclude these trials from the rest of this work.

The secondary nucleation rate is presented in Fig. 12 for both crystallizers.



Fig. 12. Parametric study on the secondary nucleation rate for both types of agitation.

The obtained orders of magnitude for the nucleation rates (between 10^2 and 10^5 s⁻¹.m⁻³) show that secondary nucleation is an intense mechanism, which seems consistent with the massive formation of nuclei observed in Fig. 8, and previously by Delgado et al. [23].

For both types of agitation, the secondary nucleation rate first increased with the supercooling degree, reached a maximum value near 75°C and then started to decrease. The nucleation rate thus seems to depend strongly on the temperature, with a progressive activation of the mechanism between 90°C and 80°C.

The influence of the stirring intensity seems again negligible. Mechanical agitation induced higher secondary nucleation rates, probably because of the shocks involved with the propeller's blades.

4.3.3 Discussion on the surface secondary nucleation

Fig. 12 shows that secondary nucleation in stirred Xylitol is a thermally activated mechanism. Tai et al. [35] showed that supersaturation is one of the primary factor in the determination of the surface nucleation rate compared to the effect of agitation, in line with previous observations of this work. Surface nucleation then seems to be responsible for most of the creation of the newly formed nuclei in the studied crystallizers. Moreover, surface nucleation is already known as the most important source of nuclei in industrial crystallizers [12]. Let us notice that Delgado et al. [23] did not study surface secondary nucleation, since they discussed crystallizations conducted at high temperatures, close to 90°C, for which the surface nucleation was a priori not activated. However, for lower temperatures, the authors reported massive formations of nuclei and a very intense phenomenon, without detailing it. Their results are thus consistent with the conclusions of this work. Besides, the authors underlined that initial breeding and attrition might not be negligible for high sample temperatures, close to 90°C.

Similarly to primary nucleation and crystal growth, the fact that the surface nucleation rate starts to decrease at low temperatures may be explained by the influence of viscosity; the low molecular diffusivity prevents molecules from reorganizing into a crystalline structure [36].

If triggering primary nucleation in Xylitol has shown to be impossible in a LHTES system, triggering surface secondary nucleation seems to be relatively easy to achieve and results in particularly high nucleation rates. Even if the metastable zone width of surface nucleation is known to be shorter than the ones of primary nucleation, it is impressive to observe such a difference in the activation of the nucleation mechanisms. To initiate as fast as possible a massive formation of secondary nuclei in a stirred LHTES system, it would then be crucial to cool down as fast as possible the PCM sample below the metastable zone width of surface nucleation. To determine more precisely this activation temperature for the design of future demonstrators, first models of the secondary nucleation rate, fitted on the present experimental points, are presented in the continuation of this work.

4.4 Modelling the secondary nucleation rate

4.4.1 Model proposal

No model for surface secondary nucleation in supercooled melts was found in literature. The nucleation rates was then modeled by adapting existing equations for crystallizations in solutions to a viscous supercooled melt.

For primary nucleation, Eq. (7) is often used to model the influence of viscosity [36]:

$$J = \frac{K}{\eta(T)} exp\left(\frac{-\Delta G^*}{k_B T}\right)$$
(7)

Where $K \approx 10^{36}$ N.m⁻⁵ is an experimental value considered independent of the temperature, η is the viscosity and ΔG^* is the activation energy to form new critical nuclei. Mullin [15] applied Eq. (7) to supercooled melts to get (Eq. (8)):

$$J = \frac{A}{\eta(T)} exp\left(\frac{-B}{T(T_m - T)^2}\right)$$
(8)

Where A and B are experimental constants (the variation in A with temperature is negligible compared to the exponential term), T is the melting temperature and $(T_m - T)$ is the supercooling degree.

On the other hand, Mersmann [37] described surface secondary nucleation as a two-dimensional nucleation mechanism on the surface S of the crystals already present in the solution. It corresponds to an activated mechanism, which kinetics is of the form [38] (Eq. (9)):

$$J_{surf} = K_{surf}.S.exp\left(\frac{-\Delta G_{surf}^*}{k_B T}\right)$$
(9)

As for Eq. (3), secondary nucleation rate was supposed constant during the induction time by considering a constant surface S for nucleation.

Assuming a similar expression of ΔG_{surf}^* and combining Eq. (8) and Eq. (9) as a first approach gives a formulation of the surface secondary nucleation in viscous melts (Eq. (10)):

$$J_{surf} = \frac{A_{surf}}{\eta(T)} \cdot exp\left(\frac{-B_{surf}}{T(T_m - T)^2}\right)$$
(10)

Where A_{surf} is a kinetic coefficient representing the intensity of the mechanism and B_{surf} is linked to the metastable zone width and the interfacial energies involved in the formation of nuclei. A_{surf} likely depends on the agitation [37].

The previous experimental values of Zhang et al. [10] were used to model the variation of the viscosity $\eta(T)$ with the Xylitol sample temperature.

4.4.2 Fitting experimental parameters

To fit the experimental parameters A_{surf} and B_{surf} , Eq. (10) was transformed into a linear function (Eq. (11)):

$$Y(X) = X.\ln(\eta J_{surf}) = X.\ln(A_{surf}) - B_{surf}$$
⁽¹¹⁾

Where
$$X(T) = T(T_m - T)^2$$

This linear function Y and its linear fitting are represented in Fig. 13 for both crystallizers and the different stirring parameters.



Fig. 13. Modelling the secondary nucleation rate – fitting the experimental parameters.

Obtained fitting parameters A_{surf} and B_{surf} and coefficient of determination R² for the model are presented in Table 3:

Table 3

Experimental fitting parameters to model surface nucleation for both crystallizers and different agitations.

	Agitation	A _{surf} (Pa.m ⁻³)	B _{surf} (K ³)	R ²
Bubbling crystallizer	1 L/min	2.2×10^{3}	3.8×10^{3}	0.96
	2 L/min	1.3×10^{4}	8.7×10^{3}	0.94
Glass crystallizer –	70 rpm	6.5×10^{4}	1.1×10^{4}	0.94
incontanioal agration	150 rpm	7.4×10^{5}	1.8×10^{4}	0.91
	300 rpm	1.9×10^{6}	1.7×10^{4}	0.94

The linear tendency of the function Y in Fig. 13 and the values obtained for R² in Table 3 seem to indicate that the model used in this work for the secondary nucleation is consistent.

The metastable zone width seems to be the same for both crystallizers and all agitation values, since the different B_{surf} obtained are very close (near 10⁴ K³). The intensity of the nucleation represented by A_{surf} increases with the agitation intensity. The mechanism also seems to be more intense in the glass crystallizer.

These observations are consistent with what was expected. The metastable zone width does not depend on the agitation intensity or the crystallizer dimensions. Moreover, it seems that increasing the agitation intensity allows to increase the nucleation rate. Although this last observation could not have been done from the experimental values, it is consistent with surface nucleation theory.

4.4.3 Comparison with experimental results

A model for the secondary nucleation rate was reconstructed using the previous fitted parameters A_{surf} and B_{surf} and Eq. (10). The obtained model is compared to the experimental values of the secondary nucleation rate in Fig. 14.

In Fig. 14, the model proposed for the secondary nucleation rate seems consistent with the experimental results; it follows the same tendency, passing by a maximum value and then decreasing due to the influence of Xylitol viscosity for temperatures below 70°C.

The different metastable zone widths seem to be very close with an activation of the model below 90°C for all the different models. However, the modeled nucleation rate reaches its maximal value too soon compared to the experimental values. Only surface nucleation mechanisms were considered in the model, whereas seeds introduced in the crystallizer were aggregates of small crystals, an important source of initial breeding and disaggregation. This may result in an increase in the measured nucleation rates for high temperatures compared to the surface nucleation rate. The surface nucleation model of this work may then have a too short metastable zone width.



Fig. 14. Modelling the secondary nucleation rate – comparison with the experimental results.

For both crystallizers, the modeled nucleation rate increases with the agitation, following A_{surf} variations. It is particularly visible for the mechanical agitation. This result indicates that increasing the agitation intensity could eventually be a relevant strategy to reduce the latency time in a real LHTES system. However, even if such an observation seems consistent with surface nucleation mechanisms [37], uncertainties in the measurement prevent from making conclusion on this second order parameter. In the end, locally cooling the seeded and stirred PCM remains the first strategy in order to initiate rapidly the crystallization

5 Conclusions

Xylitol is a promising PCM for low temperature applications. However, it presents a high and persistent supercooling and a very low crystal growth rate, making it hard to crystallize. The development of a crystallization triggering technique creating many nuclei in the supercooled PCM would be necessary for the design of a real heat storage device using Xylitol. If bubbling and stirring were already known as promising methods, the nucleation mechanisms involved were not clearly understood. This article aimed to provide a better understanding of this process, to improve existing solutions and to propose first models for the design of future demonstrators.

First, Xylitol primary nucleation has shown to be impossible to trigger by stirring or shearing in reasonable timescales for a LHTES application. Therefore, secondary nucleation was proposed as the main source of nuclei in stirred melts; the agitation rips off crystalline particles from pre-existing crystals and disperse them in the stirred volume of PCM. However, this mechanism requires the presence of the crystalline phase in the stirred supercooled melt. Thus, triggering Xylitol by stirring might be possible thanks to unintentional seeding issues, leading to unreproducible induction times. Therefore, it has been shown that adding a seeding step to the discharge protocol, injecting crystalline Xylitol powder in the supercooled stirred melt, allows to control and speed up the Xylitol crystallization and to get reproducible results.

Among the different secondary nucleation mechanisms described in literature, the nuclei formed in the stirred crystallizers probably came from surface nucleation. Indeed, the measured secondary nucleation rates were strongly influenced by the sample temperature rather than the agitation intensity, which goes in favor of a thermally activated mechanism. A first model of the surface nucleation rate in stirred Xylitol was also proposed, with promising results. Secondary surface nucleation then appeared to be a very promising mechanism to trigger Xylitol crystallization.

Bubbling being easier to implement in a real LHTES system, the integration of a crystallization triggering technique coupling bubbling and seeding in a LHTES demonstrator using Xylitol as PCM would be a logical continuation of the present work. Moreover, future works might focus on providing models for the surface secondary nucleation that take into account the influence of the seeds quality on the induction time in order to keep optimizing the seeding protocol.

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