Research Papers

# Thermal endurance of xylitol as a phase change material for thermal energy storage applications

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A B S T R A C T

Xylitol shares the good thermophysical properties of other sugar alcohols that are candidates for thermal storage purposes, with one singularity: it shows noticeable supercooling coupled with a low crystallization rate. This makes it a suitable material for long-term heat storage applications based on supercooled PCMs, but its thermal endurance for TES purposes remains unknown. Accordingly, a stability test was performed, which consisted of placing several tubes with fresh xylitol inside a heating cabinet, where they remained under isothermal conditions for periods of up to 150 days. Both open and closed (tight) tubes were employed under various test temperatures. Samples were afterwards analyzed by differential scanning calorimetry, X-ray diffraction and high performance liquid chromatography. The thermal properties and structure of the material remained stable during the 150 days of the test at 10 °C above its melting point, while at higher temperatures degradation was observed in the material over shorter periods. The behavior is noticeably better than the thermal endurance of other sugar alcohols reported in the literature, such as mannitol, dulcitol, erythritol and inositol.

## 1. Introduction

Thermal energy storage (TES) allows the decoupling of energy supply and demand and is, therefore, essential for the efficient operation of intermittent thermal energy generation applications, such as solar thermal and others. Amongst the different types of TES available, latent heat thermal energy storage (LHTES) systems offer an interesting alternative to conventional sensible TES solutions, since they can provide increased energy density [1]. They rely on the use of phase change materials (PCMs) as a storage medium; these PCMs store the energy as latent heat of fusion and release it during crystallization. Due to the use of a phase change process, the heat is absorbed and released at a nearly constant temperature, which can be beneficial for energy applications [2].

Any PCM for LHTES has to meet specific characteristics. Based on general selection criteria [2], it can be stated that polyols (or sugar alcohols) comprise a group with remarkable potential for low-to-medium temperature TES applications (50 to 250 °C) [3]. They are safe, biodegradable, extracted from sustainable sources and are reasonably priced. They possess high mass-specific and volume-specific phase change enthalpies in comparison to other PCMs [4]. They show various melting temperatures suitable for different applications (see Table 1) and their mixtures can provide additional melting temperatures if required [3,5,6]. Besides, even though some of them show kinetic-related issues, such as polymorphism [5,7] and low crystallization rates [5], solutions have been proposed to mitigate them [8–10].

According to the literature, their main shortcoming might come from their low thermal endurance [12], especially for certain compounds [13]. Due to their polyhydric structures, most sugar alcohols tend to form ketones or aldehydes when exposed to oxygen, especially at high temperatures [14]. This problem has been evaluated in previous articles, which have mainly been focused on the thermal stability of four sugar alcohols: D-mannitol [15–18], dulcitol (or galactitol) [13], myo-inositol [14,19] and erythritol [14], along with trials to improve it. Some of their eutectic mixtures have been also tested [14,20]. All the consulted references agree in concluding that the thermal endurance of these four compounds is an important issue. However, to the best of the authors' knowledge, the thermal endurance of xylitol for TES purposes remains unknown.

Xylitol shares the good thermophysical properties of the mentioned

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**Table 1**

Thermal properties of the pure sugar alcohols considered as main candidates for TES, retrieved from [11].

| PCM | Melting temperature (°C) | Phase change enthalpy (kJ/kg) |
| --- | --- | --- |
| Myo-inositol | 224.3 ± 0.2 | 258.3 ± 1.6 |
| Dulcitol | 185.9 ± 0.2 | 334.1 ± 0.6 |
| Mannitol | 166.1 ± 0.0 | 281.0 ± 1.8 |
| Erythritol | 118.9 ± 0.1 | 332.3 ± 0.8 |
| Xylitol | 93.3 ± 0.2 | 237.5 ± 3.5 |
| Sorbitol | 97.4 ± 0.2 | 164.0 ± 3.2 |

**Table 2**

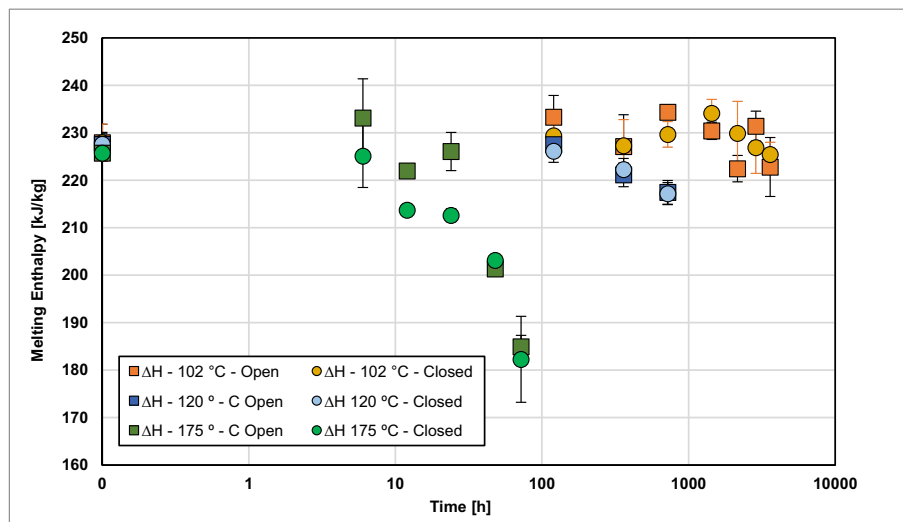Thermal endurance test temperatures and sample times.

| Test temperature | Temperature increase regarding melting point | Time of the thermal endurance test |
| --- | --- | --- |
| 102 °C | 10 °C | 5, 15, 30, 60, 120 and 150 days. |
| 120 °C | 28 °C | 5, 15 and 30 days. |
| 175 °C | 83 °C | 6, 12, 24, 48 and 72 h. |
| 250 °C | 158 °C | 6, 24, 48 and 72 h. |

sugar alcohols (see Table 1) with one singularity: it shows a noticeable and stable supercooling coupled with a low crystallization rate [5,9]. This leads to difficulties to nucleate on cooling and, when it does, it shows a low release rate of the stored latent heat, which can be a limiting factor for typical LHTES systems. However, the problem has been
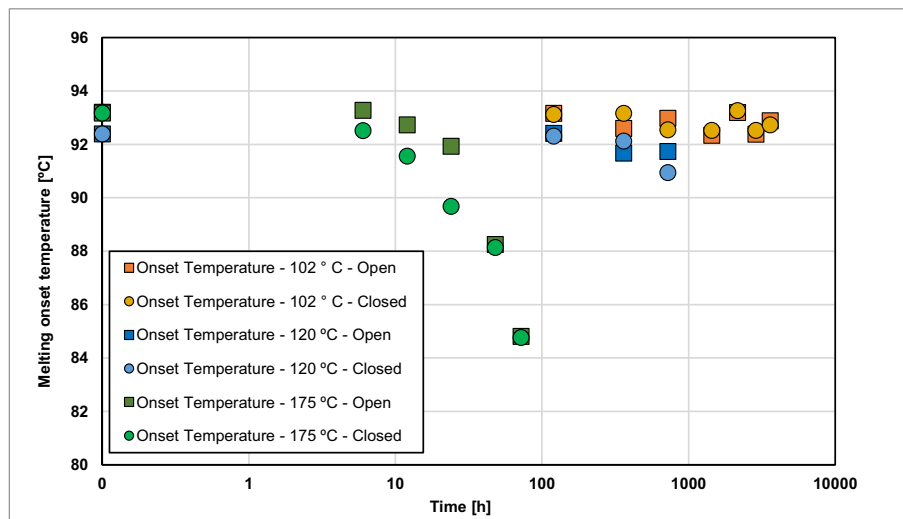
**Table 3**

Melting enthalpies obtained for the samples of the thermal endurance test at 102 °C.

| Melting enthalpy [kJ/kg] | | | | | |
| --- | --- | --- | --- | --- | --- |
| Time [days] | Time [h] | Open tubes | | Closed tubes | |
| | | Average | Standard deviation | Average | Standard deviation |
| 0 | 0 | 227.9 | 3.9 | 227.9 | 3.9 |
| 5 | 120 | 233.3 | 4.5 | 229.4 | 3.9 |
| 15 | 360 | 227.1 | 6.7 | 227.3 | 5.5 |
| 30 | 720 | 234.3 | 1.2 | 229.7 | 2.7 |
| 60 | 1440 | 230.4 | 2 | 234.1 | 2.9 |
| 90 | 2160 | 222.5 | 2.8 | 229.9 | 6.7 |
| 120 | 2880 | 231.4 | 3.2 | 226.9 | 5.4 |
| 150 | 3600 | 222.8 | 6.2 | 225 | 2.6 |



**Fig. 1.** Evolution of the obtained melting enthalpies for the samples of the thermal endurance test at 102, 120 and 175 °C (abscissae presented in log scale).



**Fig. 2.** Evolution of the obtained melting onset temperatures for the samples of the thermal endurance test at 102, 120 and 175 °C (abscissae presented in log scale).

**Table 4**
DSC melting onset temperatures obtained for the samples of the thermal endurance test at 102 °C.

| Melting onset temperature [°C] | | | | | |
|---|---|---|---|---|---|
| Time [days] | Time [h] | Open tubes | | Closed tubes | |
| | | Average | Standard deviation | Average | Standard deviation |
| 0 | 0 | 93.2 | 0.1 | 93.1 | 0.1 |
| 5 | 120 | 93.2 | 0.4 | 92.7 | 0.1 |
| 15 | 360 | 92.6 | 0.2 | 92.8 | 0.2 |
| 30 | 720 | 93.0 | 0.0 | 92.4 | 0.7 |
| 60 | 1440 | 92.3 | 0 | 92.4 | 0.2 |
| 90 | 2160 | 93.2 | 0.4 | 92.3 | 0.3 |
| 120 | 2880 | 92.4 | 0.2 | 92.5 | 0.1 |
| 150 | 3600 | 92.9 | 0.6 | 92.7 | 0.6 |

overcome with nucleation-triggering technologies, such as stirring by bubbling [21] and/or mechanical shearing [8]. Both techniques can promote a fast crystallization of xylitol. Indeed, thanks to its particular behavior and the developed triggering techniques, xylitol is a promising candidate for medium and long-term heat storage applications based on supercooled PCMs [22]. In these applications, the PCM remains in the supercooled state until the heat release is required. Then, crystallization is promoted on-demand by an external stimulus [23,24].

As a result, xylitol has recently gained an important visibility. However, even though previous articles [9] mention that its thermal properties do not decline with a large number of melting–crystallization cycles, the only article found in the performed literature survey that includes experimental results related to thermal endurance was recently published by Delgado et.al [8]. Within a rheological investigation of the acceleration of xylitol crystallization by shearing, they evaluated the thermal stability of xylitol after it underwent a shearing process in a rheometer during 1500 s at 90 °C. The performed post-mortem assessment found no significant differences between the fresh and the sheared xylitol.

This shortage of stability related studies in the literature is probably due to the singular crystallization behavior of xylitol: since it does not readily crystallize, it is not possible to perform an accelerated thermal cycling analysis, which is typically used to preliminarily evaluate the thermal stability of PCMs [13,25]; alternative procedures are required. Accordingly, in the present article, an evaluation test maintaining the xylitol under isothermal conditions for several days/months at various temperatures above its melting point is presented. After the corresponding test period, each sample was extracted, crystallization was promoted by shearing and its degradation was assessed by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and high performance liquid chromatography (HPLC). Finally, the obtained results were compared with the stability of other sugar alcohols previously reported in the literature.
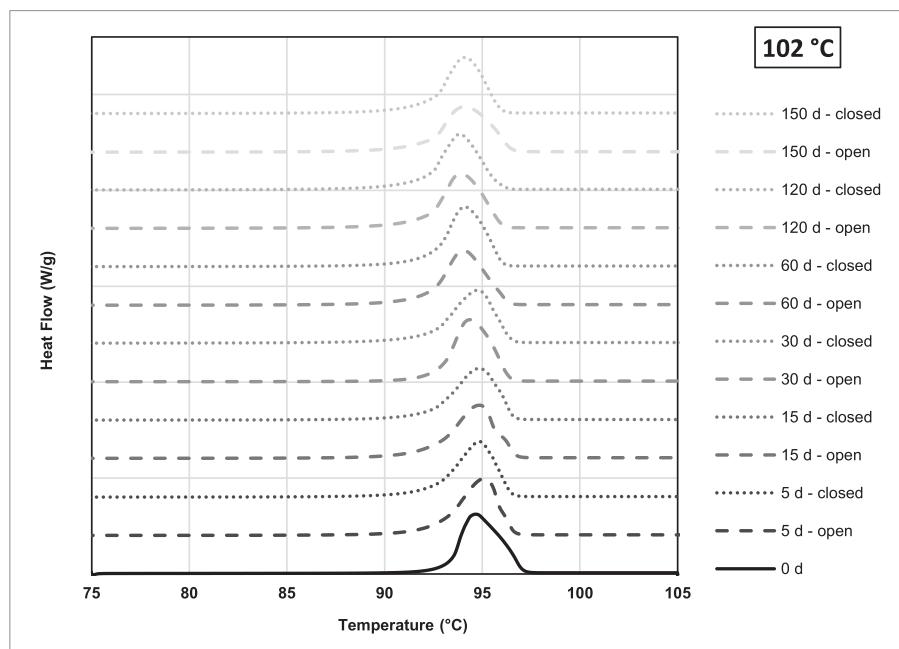
**Table 5**
Melting enthalpies for the samples of the thermal endurance test at 120 °C.

| Melting enthalpy [kJ/kg] | | | | | |
|---|---|---|---|---|---|
| Time [days] | Time [h] | Open tubes | | Closed tubes | |
| | | Average | Standard deviation | Average | Standard deviation |
| 0 | 0 | 227.6 | 2.5 | 227.6 | 2.5 |
| 5 | 120 | 227.5 | 1.1 | 226.1 | 1.4 |
| 15 | 360 | 221.1 | 3.0 | 222.3 | 1.6 |
| 30 | 720 | 217.5 | 5.4 | 217.2 | 1.2 |

**Table 6**
DSC melting onset temperatures for the samples of the thermal endurance test at 120 °C.

| Melting onset temperature [°C] | | | | | |
|---|---|---|---|---|---|
| Time [days] | Time [h] | Open tubes | | Closed tubes | |
| | | Average | Standard deviation | Average | Standard deviation |
| 0 | 0 | 92.4 | 0.2 | 92.4 | 0.2 |
| 5 | 120 | 92.4 | 0.2 | 92.3 | 0.0 |
| 15 | 360 | 91.7 | 0.5 | 92.1 | 0.5 |
| 30 | 720 | 91.7 | 1.1 | 90.9 | 0.2 |



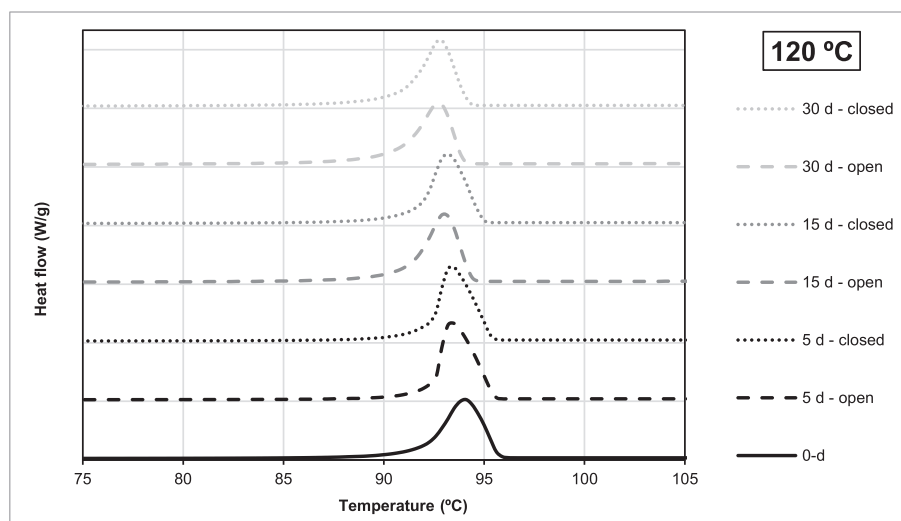**Fig. 3.** DSC thermograms obtained for tested samples of the thermal endurance test at 102 °C.

**Fig. 4.** DSC thermograms obtained for tested samples of the thermal endurance test at 120 °C.

**Table 7**
Melting enthalpies for the samples of the thermal endurance test at 175 °C.

| Melting enthalpy [kJ/kg] | | | | |
|---|---|---|---|---|
| Time [h] | Open tubes | | Closed tubes | |
| | Average | Standard deviation | Average | Standard deviation |
| 0 | 225.7 | 0.9 | 225.7 | 0.9 |
| 6 | 233.2 | 8.2 | 225.1 | 6.6 |
| 12 | 222.0 | 0.9 | 213.7 | 1.2 |
| 24 | 226.1 | 4.0 | 212.6 | 1.4 |
| 48 | 201.3 | 0.3 | 203.1 | 1.2 |
| 72 | 185.0 | 2.4 | 182.3 | 9.1 |

**Table 8**
DSC melting onset temperatures for the samples of the thermal endurance test at 175 °C.

| Melting onset temperature [°C] | | | | |
|---|---|---|---|---|
| Time [h] | Open tubes | | Closed tubes | |
| | Average | Standard deviation | Average | Standard deviation |
| 0 | 93.2 | 0.1 | 93.2 | 0.1 |
| 6 | 93.3 | 0.0 | 92.5 | 0.8 |
| 12 | 92.7 | 0.1 | 91.6 | 0.1 |
| 24 | 91.9 | 0.1 | 89.7 | 0.1 |
| 48 | 88.2 | 0.05 | 88.1 | 0.3 |
| 72 | 84.8 | 0.2 | 84.8 | 0.2 |

## 2. Materials and methods

Analytical grade xylitol (Sigma Aldrich, CAS number: 87-99-0, ref. product: W507930) with a purity of ≥97.5 % was used. Its main thermal characteristics were measured by DSC, following the procedure explained in Section 2.2. The material showed an average melting onset temperature of 93.1 °C and melting latent enthalpy of 228 J/g.

### 2.1. Thermal endurance test

The performed thermal endurance test consisted of introducing several tubes with fresh xylitol inside a heating cabinet, where the samples were maintained under isothermal conditions during variable periods. The employed containers consisted of stainless steel tubes 100 mm in length and 12 mm in diameter. They were positioned vertically inside the heating cabinet, held by a rack. Open and closed tubes were

used, in order to compare the influence of tightness in the thermal endurance. To close the tubes, a threaded plug was placed at the ends of each tube combined with sealing ferrules, both also made of stainless steel. A tight container was therefore obtained. The open tubes did not include this closing system at their top.

To prepare the samples, approximately 6 g of xylitol powder were introduced into the tubes and the ends were closed. Xylitol was maintained in a desiccator with phosphorus pentoxide for 3 days before it was inserted in the tubes, in order to ensure the absence of moisture. The tubes were weighed (±0.001 mg) before and after the endurance test to analyze any mass loss. In order to duplicate the measurements, 2 tubes were prepared per time analyzed and per configuration (open and closed).

The test temperatures and the time that elapsed with the samples under the corresponding conditions are shown in Table 2. At lower temperatures, a reduced degradation was observed (see Section 3), so the maximum test duration was of the order of months; this was not necessary for 175 °C and 250 °C, where degradation was already significant after only several hours of test.

Once each tube had been extracted from the cabinet at the times specified in Table 2, the xylitol was extracted by means of a spatula. The material was a viscous liquid, even though its temperature was below its solidification temperature. Pressure and shearing was applied manually by means of a small metallic stick and crystallization occurred. The solid samples were stored in a desiccator at room temperature for later analysis.

The agreement between the temperature of the used heating cabinet and the samples was verified by a Pt-100 probe during the test performed at 102 °C. The probe was inserted in one of the open tubes filled with xylitol and connected to a data acquisition system (this was an additional sample and was not analyzed afterwards). Data were obtained every 30 s. The average temperature registered within the tube was 101.9 °C, with a standard deviation of 0.35 °C. The temperature correspondence between the heating cabinet and samples can be considered suitable for the intended purposes.

Bearing into mind that the scope of the article is to evaluate the degradation under conditions representative of applications based on supercooled PCMs, the selected type of endurance test was preferred over another typical alternatives such as a kinetic evaluation by TGA. The used sample mass is more representative (grams instead of mg); both open and closed containers were evaluated (the latter cannot be assessed by TGA) and an isothermal temperature program was applied, which is more representative for the intended application than the typical TGA dynamic segments. The selected test type was also
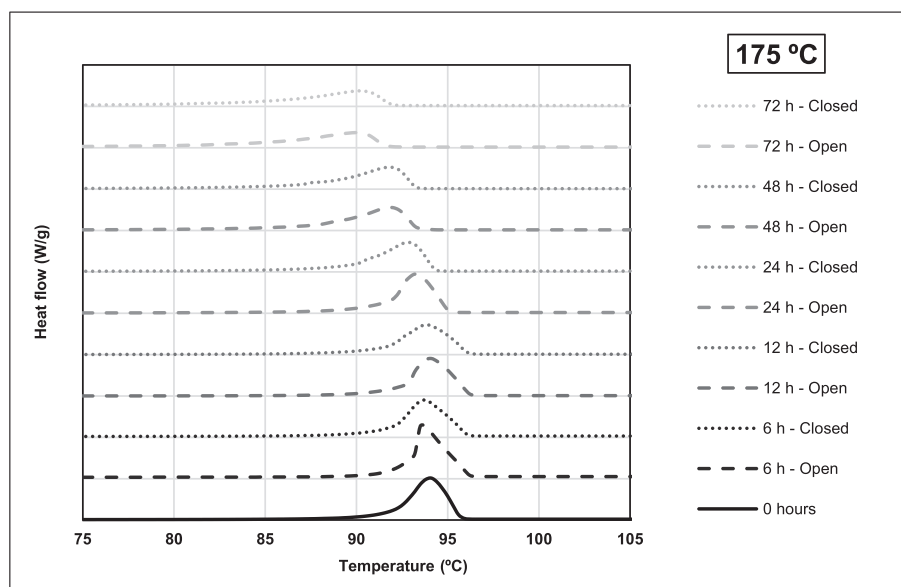
**Fig. 5.** DSC thermograms obtained for tested samples of the thermal endurance test at 175 °C.
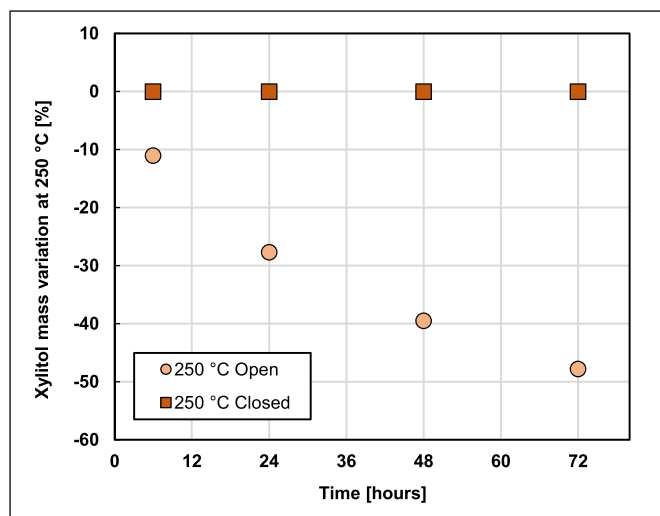


**Fig. 6.** Mass variation during the endurance tests for samples at 250 °C.

considered more representative than accelerated thermal cycling analysis, which besides could not be easily applied due to the singular crystallization behavior of xylitol.

### 2.2. Analytical evaluation of the samples

The main features of the DSC, XRD and HLPC devices used are detailed next, along with the employed operation methods.

#### 2.2.1. Differential scanning calorimetry

DSC (model: DSC1 from Mettler Toledo) was used to assess the main thermal properties of xylitol before and after the endurance test. Heat flow and temperature calibrations were carried out with both gallium and indium. Sealed aluminum crucibles of 25 μL were used and dry nitrogen (99.999 %) was employed as both protective and purge gas. To prepare the DSC samples, an aliquot of 5–10 mg of the solid xylitol extracted from the tubes and subsequently stored in glass vials was gently ground in an agate mortar, weighed (±0.001 mg) and inserted into the crucibles. Two samples per tube were analyzed.

The employed temperature program consisted of a heating ramp from 50 to 110 °C at 2 °C/min. Isothermal segments of 5 min were applied before and after the ramp to homogenize the temperature of the sample. Since xylitol does not crystallize on cooling unless an external stimulus is applied, a unique heating segment was applied to study the sample upon melting, with no subsequent solidification.

For the analysis, phase change enthalpies were determined by the integration of the melting peak of the thermograms. Accordingly, the reported enthalpies consider only latent heat. An integral tangential interpolated baseline was used. The melting temperature of the samples was established by the onset temperature of the thermograms.

#### 2.2.2. X–ray diffraction (XRD)

X–ray diffraction (XRD) was employed to assess any modification in the solid crystalline phases of xylitol. Measurements were performed at ambient temperature. The diffraction patterns were collected using a Philips X'pert Pro automatic diffractometer. It operated at 40 kV and 40 mA in theta-theta configuration using a secondary monochromator with Cu-Kα radiation (λ = 1.5418 Å), and a PIXcel solid-state detector (active length in 2θ 3.347°). Data were gathered from 10 to 80° 2θ (step size = 0.026° and time per step = 120 s). A fixed divergence and anti-scattering slit that gave a constant volume of sample illumination were employed. Identification of the solid phases present in the mixture was performed using the Powder Diffraction File (PDF) database. The PANalytical X'Pert High Score program was used for identification and Miller indexing of all observed maxima.

#### 2.2.3. High performance liquid chromatography (HPLC)

HPLC was employed to quantify the remaining content of xylitol in the samples submitted to the thermal endurance test. Measurements were performed on an Agilent 1260 series HPLC system supplied with a binary pump coupled to a refractive index detector (RID) Agilent 1260 from Agilent Technologies (Santa Clara, CA, USA) operating at 45 °C. The column used was an Eclipse Rezax RCM-Monosaccharide Ca+2, with water Milli-Q as mobile phase at 0.5 mL/min. The column temperature was maintained at 80 °C.

For quantification, a calibration curve was prepared using various solutions of the pristine compound, with concentrations from 100 to 5500 mg/L. The calibration curve was fitted by linear regression, obtaining a correlation coefficient of 0.998. To prepare each HPLC sample, a xylitol aliquot extracted from the thermal endurance tubes
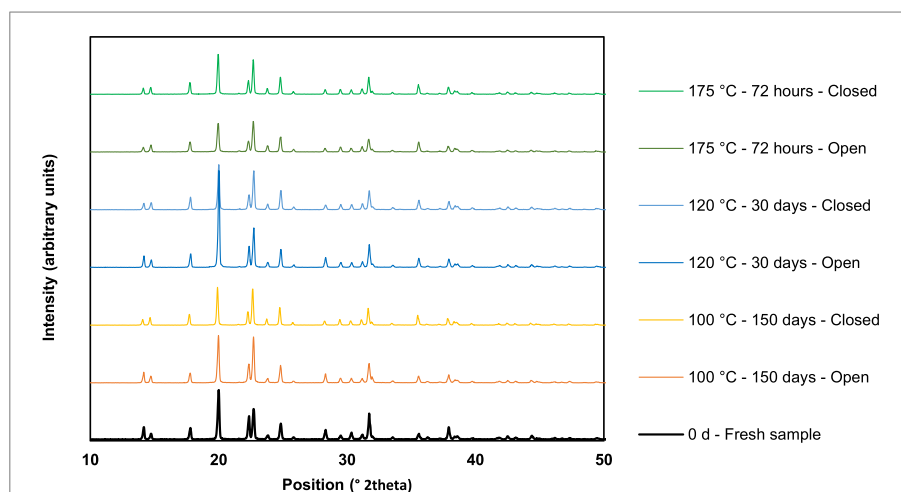
**Fig. 7.** XRD diffractograms obtained for fresh xylitol and for samples after the endurance test at 102, 120 and 175 °C.
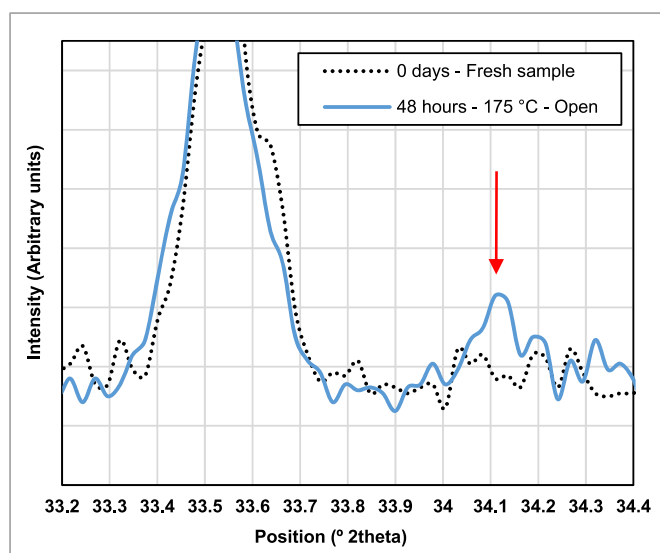


**Fig. 8.** Detailed view of the unmatched new diffraction observed in all samples from the endurance test at 175 °C (the position of the new peak is indicated by the red arrow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

was ground in an agate mortar and approximately 20 mg were dissolved in 10 mL of distilled water. The chromatographic signal for xylitol was obtained at a retention time of around 27 min.

## 3. Results and discussion

The results section starts with the thermal analysis of the samples, followed by the mass loss, XRD and HLPC. The color change is discussed next. Finally, a comparison of the thermal endurance with other sugar alcohols is provided.

### 3.1. Thermal analysis of the samples (DSC)

The evolution of the latent melting enthalpies of xylitol at different test temperatures is provided in Fig. 1; while the melting onset temperatures are presented in Fig. 2 (note that the abscissae in both cases are plotted in a logarithmic scale). Each point in the figures represents the average result of the 4 samples of each experimental condition and

the error bars represent the standard deviation of the samples that comprise every point. The results are discussed along the following subsections, broken down by temperatures and supported by tables that provide numerical information.

Note that the samples kept at 250 °C turned into a viscous black liquid even after only 6 h. These samples did not crystallize under shearing or grounding after they were extracted from the heating cabinet, even though various attempts were performed. Although some DSC samples were prepared with the formed viscous substance, the thermograms did not show any melting peak; thus, no thermal analysis results are available at those temperatures.

#### 3.1.1. Thermal properties of samples maintained at 102 °C

The latent melting enthalpy numerical results for the endurance test at 102 °C (10 °C above the melting temperature of xylitol) are provided in Table 3. For both open and closed tubes, no significant decreasing trend was noticed during the 150 days of the test. The difference between the initial and final melting enthalpies was 5 J/g for open tubes and 3 J/g for closed ones. These values represent a relative decrease of <2 %, which can be considered within the acceptable accuracy reported for DSC measurements in PCMs (~4 % in enthalpy) [26].

Note that the decrease in the registered enthalpy was not monotonic. A slight enthalpy increase was observed in certain samples (e.g.: 60 days) compared to 0 days. This effect was attributed to the different degree of crystallization attained when preparing xylitol samples from the melt by manual grinding. In order to account for this effect, the difference between the maximum and minimum enthalpy registered during the endurance test was also evaluated. From the data in Table 3, it can be extracted that this difference was 9.1 J/g for closed tubes, which represents a relative deviation of 4 % compared with the obtained maximum enthalpy value. Similar results were achieved for open tubes.

The obtained DSC melting onset temperatures are numerically presented in Table 4 (also illustrated in Fig. 2). A slight decrease of 0.3 and 0.4 °C, respectively, was noticed for both open and closed containers after 150 days. Even though this difference is larger than the accuracy of the employed DSC (±0.2 °C), the change is minor and would not significantly affect the performance of xylitol in an actual thermal storage system.

To complement these results, the melting DSC thermograms of certain samples are provided in Fig. 3. As observed, the shapes of the heat flow signal remained alike during the test for both open and closed systems; no new transitions or peaks appeared during the 150 days of thermal endurance test. The endset temperatures of the thermograms showed slight variations, but with no clear trend; thus, this is most likely due to the different sample mass employed within the DSC crucibles,
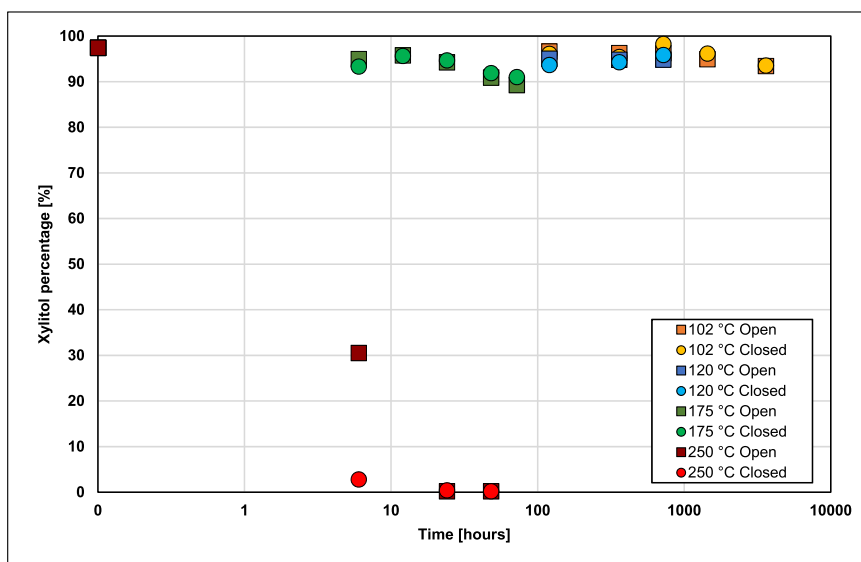
**Fig. 9.** HPLC results of the samples tested under all temperatures: 102, 120, 175 and 250 °C (abscissae are plotted in log scale).



**Fig. 10.** Color evolution of the samples after the thermal endurance test (solid state): a) fresh xylitol; b) xylitol maintained at 100 °C during 150 days; c) xylitol maintained at 120 °C during 30 days and d) xylitol maintained at 175 °C during 72 h.



**Fig. 11.** Color evolution of the samples after the thermal endurance test (supercooled liquid state): a) xylitol maintained at 100 °C during 150 days; b) xylitol maintained at 120 °C during 30 days; c) xylitol maintained at 175 °C during 72 h and d) xylitol maintained at 250 °C during 72 h.

which ranged from 5 to 8 mg (remember that, contrary to onset temperatures, endset temperatures in DSC are dependent on sample mass and measurement rate).

### 3.1.2. Thermal properties of samples maintained at 120 °C

In Tables 5 and 6, the numerical results of the thermal analysis of samples kept at 120 °C during the endurance test are presented. Regarding the latent melting enthalpy evolution, unlike the samples at 102 °C, a monotonic decreasing trend was noticed (see Fig. 1). The maximum enthalpy value was registered at 0 days and decreased by 10 J/g after the studied 30 day period, for both open and closed tubes. This represents a decrease of 4.5 % regarding the initial value.

The melting onset temperatures also showed a monotonic decrease in their values. The reduction after 30 days was 0.7 °C for open tubes and 1.5 °C for the closed ones. This difference is larger than that at 102 °C for the same time period. In addition, the evolution of the melting DSC thermograms can be observed in Fig. 4. Even though the shape of the melting peak remained regular during the 30 days of the test, with no
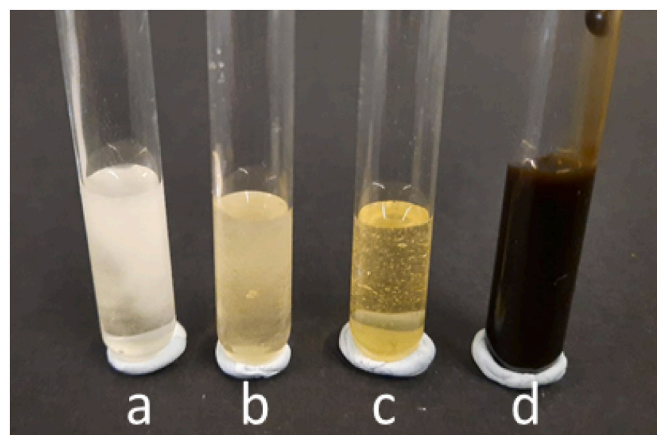
new thermal events or peaks, the endset temperatures progressively moved to lower temperatures.

The observed changes in the thermal properties after 30 days at 120 °C can be considered minor for actual storage systems; however, compared with the behavior at 102 °C, they suggest the beginning of a decrease in the thermal performance of xylitol.

### 3.1.3. Thermal properties of samples maintained at 175 °C

The DSC numerical results of the samples maintained at 175 °C are provided in Tables 7 and 8. For those samples in closed tubes, the enthalpy values decreased monotonically during the 72 h of the endurance test; meanwhile, for open tubes, the values at 6 and 24 h showed a slight increase compared with the initial enthalpy value. In any case, after 48 h the decrease between the initial and final enthalpy became evident: 40.7 and 43.4 J/g for open and closed tubes, respectively. This difference represents >15 % regarding the original value and is noticeably larger than samples at 102 and 120 °C for the same time period (see Fig. 1). These results would imply a significant decrease in the performance of the material in actual thermal storage systems.

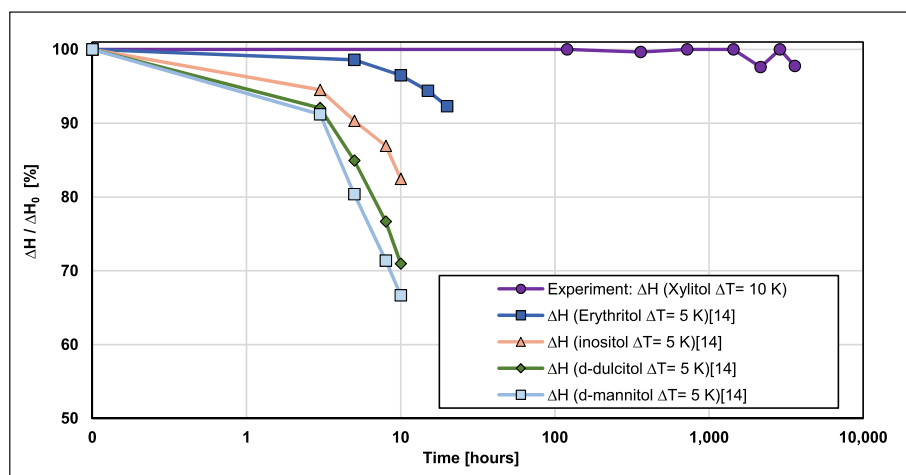The noticed drop in the melting enthalpy was reinforced with the

**Fig. 12.** Decrease in the melting enthalpies of erythritol, inositol, mannitol and dulcitol (obtained from [14]) during endurance tests at 5 °C above their melting temperature; comparison with the results attained herein for xylitol during tests at 10 °C above its melting temperature.
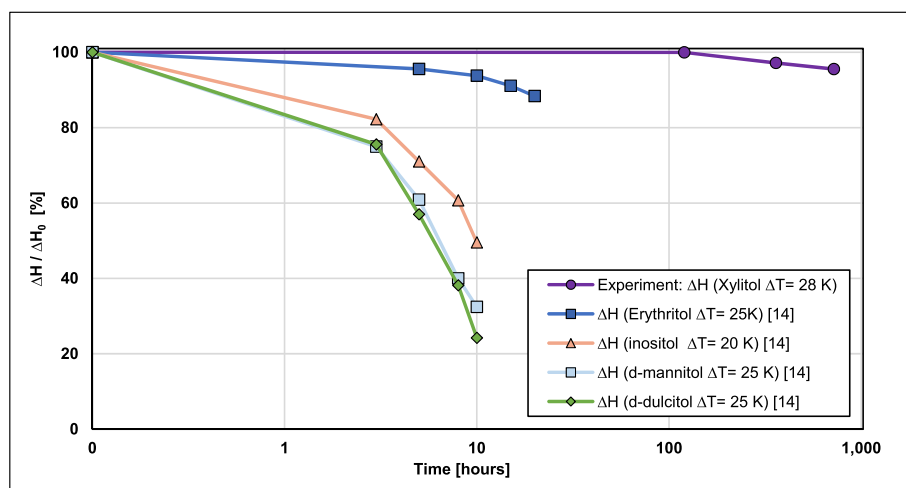


**Fig. 13.** Decrease in the melting enthalpies of erythritol, inositol, mannitol and dulcitol (obtained from [14]) after thermal endurance tests at 25 °C above their melting temperature (the inositol results were provided for a 20 °C temperature difference). Comparison with results of xylitol during tests at 28 °C above its melting temperature.

evolution of the melting onset temperatures (Table 8), which showed a decrease of 5.4 °C after 72 h for both open and closed systems. This is noticeably larger than the results at lower test temperatures, as can be appreciated in Fig. 2. The degradation effect can also be clearly inferred from Fig. 5, where the DSC thermograms are presented. The melting peaks displace to lower temperatures for increasing endurance test times and they become broader and flattened.

### 3.2. Mass loss

The weight of the xylitol was measured for every tube before and after the endurance tests in the heating cabinet. The mass variation for the samples at 102 °C and 120 °C was negligible for the whole time period (below 0.1 % of mass change). For samples at 175 °C, the mass loss was negligible for the closed tubes, while a decrease of 1 % was noticed for open tubes after 72 h. For samples at 250 °C within closed tubes, the mass loss was again negligible; however, the open tubes showed a significant mass loss of approximately 50 % of the weight after 72 h (Fig. 6). The comparison between the open and closed tubes for this last temperature demonstrates that the closed tubes were completely tight.

Considering that, overall, the decrease in the thermal properties

observed at 175 °C in Section 3.1 was similar for open and closed tubes, these mass loss results indicate that the use of a tight thermal storage container would not avoid the chemical reactions undergone by the xylitol when exposed to the mentioned temperatures; at least not under an air atmosphere as is employed here.

### 3.3. X-ray diffraction

The stability of xylitol was also assessed by XRD. Samples from every tested tube were analyzed; however, for the sake of brevity, only the patterns of the first and last samples at every temperature are provided in the discussion throughout this section. As occurred with the DSC measurements, the samples maintained at 250 °C could not be measured by XRD, due to their inability to crystallize after 6 h of endurance test.

The XRD patterns are shown in Fig. 7, for both open and closed systems. At first sight, no significant differences can be observed for any temperature between the original samples and the tested ones, which points towards no major changes in the crystalline phases present in the samples.

To complement this visual inspection, an identification of the solid phases was carried out using the Powder Diffraction File (PDF) database. For all the samples from endurance tests at 102 and 120 °C, every

diffraction peak matched those present in the xylitol pattern used as a reference (PDF Ref. code: 00-034-1802). This indicates that no significant quantities of new crystalline compounds or by-products were formed at these temperatures.

At 175 °C, however, the samples from the endurance tests did show a difference: a new peak at 34.1°2θ was found, with a relative intensity of 0.82 %. A detailed view of the peak is provided in Fig. 8. Despite its low intensity, this diffraction was present in all the samples at 175 °C and did not match the xylitol PDF pattern; therefore, its appearance suggests the formation of a new crystalline compound that was not present at lower temperatures. No successful phase identification was accomplished with other compounds within the PDF database; nonetheless, this is an expected outcome, considering that the signal comprised a standalone peak. The modification of the XRD pattern is minor, so the concentration of the newly formed compound is expected to be low; however, the finding agrees with the analysis performed in Section 3.1, where the thermal properties at 175 °C decreased noticeably more than at 102 and 120 °C.

### 3.4. High performance liquid chromatography

HPLC was performed to evaluate the mass ratio of xylitol in the samples after the thermal endurance test. In contrast to XRD, HPLC results can provide valuable information about the presence of non-crystalline impurities. The results are depicted in Fig. 9. Again, the ordinate axis is represented in logarithmic scale. Note that the identification of the potentially formed new compounds is beyond the scope of this article; their presence was inferred by means of the quantification of the concentration of xylitol in samples.

The first significant aspect in the results is the great difference between the degradation at 250 °C and the other temperatures. After only 6 h at 250 °C, the xylitol concentration in samples within closed tubes dropped to 30 %. The decay for samples from open tubes was even more severe and decreased to 5 %. After 24 h, no xylitol remained in the samples. This is consistent with the findings previously described in Section 3.1: the changes in the composition at 250 °C were so significant that the resultant material turned into a viscous black liquid even after only 6 h. Remember that these samples could not be measured by DSC or by XRD, due to the lack of crystallization even at room temperatures.

At 175 °C, the results showed a more moderate drop: the concentration steadily decreased from the original value to 89 % mass ratio after 72 h for both open and closed tubes. This agrees with the DSC results, which showed a perceptible but still minor decay in the thermal properties. It is also coherent with the XRD patterns, which showed a diffractogram formed mainly by xylitol, combined with the potential minor presence of a new, unidentified crystalline compound.

Finally, the concentration of samples for 120 and 102 °C did not show a distinctive decay. The original concentration values rendered a mass ratio of around 96 % (remember the original purity of the used xylitol was 97.5 %) and the final concentration values were maintained at above 94 % after 30 and 150 days. The results were similar for the open and closed tubes and they were consistent with the thermal analysis results and the XRD findings.

### 3.5. Color evolution of the samples

The color evolution of the samples in the solid state (powder) is shown in Fig. 10. At a plain sight, no differences could be perceived between the powder of the samples at that had been tested at 100 and 120 °C, while those samples tested at 175 °C showed a slight yellowish tone (although it is not distinguishable in Fig. 10). Besides, it was noticed that the samples tested at 175 °C were softer when they were grounded. The samples at 250 °C did not crystallize after the thermal endurance test, so they are not shown in the figure.

In Fig. 11, the color evolution of the samples in the liquid state can be visualized. To take the picture, the samples stored in the powder state

after the thermal endurance test were melted inside the heating cabinet at 100 °C for 30 min and poured into glass tubes. The picture was taken when the samples reached room temperature again.

The color changes are significant in this supercooled liquid state. The samples from the thermal endurance test at 100 °C still showed a transparent/white color, while those samples tested at 120 and 175 °C turned into a yellow liquid. The material that had been tested at 250 °C turned into a black viscous liquid. This color evolution is consistent with the results discussed along the previous sections.

### 3.6. Comparison of the thermal endurance of xylitol with other sugar alcohols reported in the literature

Shao et al. [14] recently published a study that gathered the thermal endurance assessment of four pure sugar alcohols (mannitol, dulcitol, myo-inositol and erythritol) and three binary eutectic mixtures formed by them. As the employed endurance test was similar to the one used herein, the melting enthalpies they obtained for the mentioned four pure sugar alcohols were compared with the results attained herein for xylitol.

In Fig. 12, the enthalpy evolution of the materials maintained at 5 °C above their melting temperatures can be observed. Since we did not perform endurance tests with the same temperature difference, the results are compared with those herein attained for xylitol at 10 °C above its melting temperature (thus under more unfavorable conditions). The results from [14] showed a clear reduction of the melting enthalpy in the four sugar alcohols studied, even for much shorter heating periods than those herein evaluated for xylitol (note that the abscissae in Fig. 12 are represented in logarithmic scale). An enthalpy reduction of ~7 % was observed for erythritol after being heated at 5 °C above its melting point for 20 h. The decay under similar superheating conditions was even worse for the other three pure sugar alcohols: after 10 h, the latent fusion heat of mannitol and dulcitol dropped by >25 % compared to their respective original values, while inositol presented a decay of around 15 % compared to its original melting enthalpy.

When it comes to the endurance tests performed with higher differences between the melting point of the materials and the test temperature, a similar trend was observed, as can be seen in Fig. 13. While xylitol maintained 95 % of its original melting enthalpy after 30 days at a temperature 28 °C above its melting point, the rest of the sugar alcohols showed a significantly more pronounced decay following only a one day test period.

Similar results of a noticeable degradation after short heating periods or a low number of DSC thermal cycles were reported in additional articles dealing with thermal stability tests of sugar alcohols, such as refs. [16,17,19]. As a consequence, it can be concluded that xylitol shows a better thermal endurance than other sugar alcohols of interest for TES purposes previously reported in the literature.

## 4. Conclusions

In the present article, a thermal endurance test was performed, which consisted of placing several tubes with fresh xylitol inside a heating cabinet, where they remained under isothermal conditions for periods of up to 150 days. Samples were afterwards analyzed by DSC, XRD and HPLC.

The DSC results showed that the melting enthalpy and onset temperature of xylitol after 150 days of heating at 102 °C (10 °C above its melting temperature) remain stable. At temperatures of 175 °C, the decay in the thermal properties is perceptible after 72 h. At 250 °C, the material completely degrades in <24 h. These results were consistent with the XRD and HPLC analyses.

The observed behavior is better than the thermal endurance of other sugar alcohols reported in the literature, such as mannitol, dulcitol, erythritol and inositol. These PCMs show a higher decay in their thermal properties under equivalent conditions, even for shorter periods of

analysis.

Overall, the decrease in the performance showed similar trends for open and closed (tight) tubes, revealing that the use of a tight container in real storage applications would not avoid the chemical reactions undergone by the xylitol when exposed to temperatures above 120 °C under an air atmosphere.

The obtained results encourage the research of xylitol as a phase change material; however, its maximum operation temperature should be maintained at 10 °C above its melting temperature. Further research should be focused on longer thermal endurance tests to confirm the observed behavior; studies on the use of protective atmospheres are also suggested.

## CRediT authorship contribution statement

**Gonzalo Diarce:** Conceptualization, Methodology, Supervision, Writing – original draft. **Ander Rojo:** Investigation, Methodology, Data curation. **Laura Quant:** Methodology, Writing – review & editing. **Lourdes Bouzas:** Investigation, Methodology. **Ana García-Romero:** Funding acquisition, Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

The authors are unable or have chosen not to specify which data has been used.

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