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Phase Change Material Selection for Thermal Processes Working under Partial Load Operating Conditions in the Temperature Range between 120 and 200 °C

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Abstract: In some processes, latent heat thermal energy storage (TES) systems might work under partial load operating conditions (the available thermal energy source is discontinuous or insufficient to completely charge the phase change material (PCM)). Therefore, there is a need to study how these conditions affect the discharge process to design a control strategy that can benefit the user of these systems. The aim of this paper is to show and perform at laboratory scale the selection of a PCM, with a phase change temperature between 120 and 200 °C, which will be further used in an experimental facility. Beyond the typical PCM properties, sixteen PCMs are studied here from the cycling and thermal stability point of view, as well as from the health hazard point of view. After 100 melting and freezing cycles, seven candidates out of the sixteen present a suitable cycling stability behaviour and five of them show a maximum thermal-stable temperature higher than 200 °C. Two final candidates for the partial loads approach are found in this temperature range, named high density polyethylene (HDPE) and adipic acid.

Keywords: thermal energy storage (TES); phase change material (PCM); partial load; thermal stability; cycling stability; health hazard; application

1. Introduction

Latent heat thermal energy storage (TES) using phase change materials (PCM) is an effective way of storing thermal energy because of its high energy storage density and the nearly isothermal melting and solidification processes at the phase change transition temperature of the PCM [1]. Many PCMs have been proposed in the literature for different temperature ranges, being the phase change temperature and phase change enthalpy, the main parameters provided by the authors [1–3]. However, the PCM should fulfill several other requirements besides the two mentioned above. Gasia et al. [4] summarized the main requirements for selecting proper TES materials and systems by classifying them into chemical, kinetic, physical, thermal, economic, environmental, and technological. Therefore, the selection procedure of a PCM becomes a crucial step for an optimum operation of the thermal process and the latent heat TES system. The critical parameters and necessary requirements for a specific process are not always easy to identify and are often in conflict with each other.

Latent heat TES systems working under partial load operating conditions as a consequence of the thermal processes with whom they are coupled (such as the ones shown in Table 1), are one of the specific cases which require a proper PCM selection. Partial load operating conditions refer to the charging and discharging processes where the PCM is not fully loaded. These conditions can be either an intrinsic characteristic of thermal processes, which may not have a continuous energy supply, such as solar thermal or industrial waste heat recovery processes, or can be used as a TES storage management tool to adapt current TES systems to the demand of the final user. Therefore, the selected PCM needs to undergo several charging and discharging processes, meaning that the selected PCM should have an acceptable cycling and thermal stability.

Table 1. Potential thermal energy processes which can operate under partial load operation conditions within the temperature range between 120 and 200 °C. Based on Gasia et al. [4].

Thermal Process	Range of Temperatures
Absorption refrigeration	From 80 to 230 °C
Adsorption refrigeration	From −60 to 350 °C
Transportation exhaust heat recovery	From 55 to 800 °C
Solar cooling	From 60 to 250 °C
Industrial waste heat recovery	From 30 to 1600 °C

Some authors did an attempt to study different critical parameters besides the phase change temperatures and enthalpies, and performed a more detailed characterization of different PCM in this temperature range [5–8]. Bayón et al. [5] studied the feasibility of storing latent heat with liquid crystals by performing different techniques such as polarized light microscopy, differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), and rheological measurements. They found that these materials showed promising results despite the fact that further investigations were required. Palomo del Barrio et al. [6] carried out a characterization of five pure sugar alcohols and three eutectic blends, evaluating their key thermal and physical properties, providing empirical equations, and comparing the values to those of most currently used PCM within the temperature range between 70 and 180 °C. Results showed the potential of sugar alcohols if issues such as thermal stability, thermal endurance and crystallization kinetics are solved. Haillot et al. [7] performed a PCM selection within the temperature range of 120–150 °C. They identified eleven candidates and studied their thermal behaviour by performing TGA and DSC analysis, before and after five cycles, coupled with a quadrupole mass spectrometer. They concluded that only few organic materials presented suitable properties to be applied in this temperature range but emphasised the importance of the measurement conditions on the results. Moreover, they suggested that further investigations concerning long-term stability should be done. Miró et al. [8] proposed a new methodology for PCM selection based on the health hazard and both the cycling and thermal stability properties. They added the health hazard analysis to evaluate the impact of PCM not only on humans but also for the facilities design and maintenance, and the thermal and cycling stability to evaluate the durability of the PCM for a certain industrial application. They applied this methodology to five different PCMs within the temperature range of 150–200 °C, and classified them according to their suitability.

The aim of the present study is the obtainment of a suitable PCM to be further used in a pilot plant experimental setup. This setup will be used to study the behaviour of a TES system coupled to thermal processes within a temperature range between 120 and 200 °C (Table 1) which work under partial load operating conditions. These conditions occur when the energy source is either intermittent or when the periodicity of the charge is adjusted according to the final user demand or the storage vessel design.

Therefore, sixteen PCMs are selected to study their suitability. The authors followed the criteria presented by Miró et al. [8] and studied the thermal and cycling stability, which is the main requirement for partial loads testing, and the health hazard. The novelty of this work is that the cycling stability has been improved by performing one hundred cycles. Moreover, the PCMs are cycled under an atmosphere which simulates the boundary conditions of the further pilot plant experimental setup testing and using a higher sample mass. Finally, the study of the health hazard has been extended by using an additional standard classification.

2. Materials Description

Based in the actual literature [2,7,9–13], the authors made a review of potential PCMs in the temperature range between 120 and 200 °C. Taking into account that the present study is aimed at selecting a candidate for further tests at a pilot plant scale, some materials were disregarded from the very beginning. For instance, salt hydrates usually present phase separation and are corrosive [9], and mixtures and metals might not be compatible with the heat exchanger material [10]. Sixteen different PCMs were selected and characterized in this paper based on their cited thermosphysical properties. These materials are listed in Table 2 along with their main thermosphysical properties from the literature and their manufacturer information.

Table 2. PCM candidates for thermal energy storage processes working under partial load operating conditions within a temperature range between 120 and 200 °C.

No.	**Material**	**Material Type**	**Thermophysical Properties**				**Manufacturer Information**	
			Phase Change Temperature (°C)		**Phase Change Enthalpy (kJ/kg)**		**Manufacturer**	**Purity (%)**
			Value	**Ref.**	**Value**	**Ref.**		
1	Benzoic acid	Aromatic hydrocarbon	121–123	[13]	114–147	[13]	PanReac AppliChem, Barcelona, Spain	>99.5
2	Benzamide	Aromatic hydrocarbon	124–127	[13]	169	[13]	Alfa Aesar, Ward Hill, MA, USA	>98
3	High density polyethylene (HDPE)	Polymeric hydrocarbon	130	[13]	211–233	[13]	Alfa Aesar, Ward Hill, MA, USA	n.a.
4	Sebacic acid	Dicarboxylic acid	130–134	[13]	228	[13]	Alfa Aesar, Ward Hill, MA, USA	>98
5	Phtalic anhydride	Dicarboxylic acid anhydride	131	[13]	159	[13]	Alfa Aesar, Ward Hill, MA, USA	99
6	Maleic acid	Dicarboxylic acid	131–140	[13]	235	[13]	PanReac AppliChem, Barcelona, Spain	>99
7	Urea	Organic compound	133–135	[13]	170–258	[13]	PanReac AppliChem, Barcelona, Spain	>99
8	Dimethyl terephthalate	Aromatic hydrocarbon	142	[13]	170	[13]	Alfa Aesar, Ward Hill, MA, USA	99
9	D-mannitol	Sugar alcohol	150	[11]	224–234	[11]	Sigma-Aldrich, St. Louis, MO, USA	98
10	Adipic acid	Dicarboxylic acid	150–152	[9]	213–260	[9]	Sigma-Aldrich, St. Louis, MO, USA	>99.5
11	Salycilic acid	phenolic acid	157–159	[2]	199	[2]	Sigma-Aldrich, St. Louis, MO, USA	>99
12	Potassium thiocynate	Inorganic salt	157–177	[12]	112–114	[12]	Sigma-Aldrich, St. Louis, MO, USA	>99
13	Hydroquinnone	Aromatic hydrocarbon	160–173	[12]	179–235	[12]	Sigma-Aldrich, St. Louis, MO, USA	>99
14	Benzanilide	Amide	161	[12]	129–139	[12]	Sigma-Aldrich, St. Louis, MO, USA	98
15	Dulcitol	Sugar alcohol	167–185	[9,13]	246–257	[9,13]	Sigma-Aldrich, St. Louis, MO, USA	99
16	2,2-Bis(hydroxymethyl) propionic acid (DMPA)	Carboxylic acid	185	[7]	289	[7]	Sigma-Aldrich, St. Louis, MO, USA	98

3. Methodology

The PCM characterization presented in this study followed the methodology proposed by Miró et al. [8], which studied and analysed the PCMs from three different approaches: health hazard, thermal stability, and cycling stability. In the present case, these analyses were done in parallel to fully characterize the materials and to give to the scientific community the data from all PCMs evaluated [14].

3.1. Health Hazard

The health hazard is studied to detect potential environmental and personal risks of the selected PCM for the specific application in which it is implemented. Therefore, results from the health hazard indicate the standards and procedures which need to be followed during the handling and operation of the selected PCM.

One of the most used systems to study the health hazard of a specific material is the material safety datasheet which is usually provided by the manufacturer. However, in this study, health hazard was evaluated first by means of the NFPA 704 standard and then complemented with the globally harmonized system (GHS) classification [15,16]. The "NFPA 704: Standard system for the identification of the hazards of materials for emergency response" is a standard which was developed by the National Fire Protection Association (NFPA) of the United States. This standard aims at visually providing the risk of many common chemicals by means of a coloured diamond. This diamond is divided in four indicators: red for flammability, blue for a health hazard, yellow for chemical reactivity, and white for special hazards. However, only the health hazard (blue) indicator was considered. Each indicator is graded from 0 to 4, with 0 being non-hazardous substances and 4 those that could cause death or major residual injuries by very short exposure.

After grading the materials from 0 to 4 according to the NFPA 704 standard, the health hazard was further specified with the GHS of classification and labelling of chemicals, which is an internationally agreed-upon system more complex than the NFPA 704 standard. This standard classifies hazard into physical, environmental and country-specific for many common chemical compounds. It also includes directions for application of the hazard communication elements: pictograms, signal words, and hazard statements. In this study, health hazard statements were considered for each material.

3.2. Thermal Stability

Thermal stability analyses are performed to study the PCM thermal decomposition within the operating temperature range of the process in which the TES system will be implemented. In the present study, the maximum thermal-stable temperature and the final degradation temperature of the materials under selection were measured and analysed by thermal decomposition experiments. The maximum thermal-stable temperature is defined as the temperature needed by the material to lose 1.5 wt.% of its composition. Moreover, the final degradation temperature is defined as the temperature achieved when the thermal-degradation process is finished.

In order to perform thermal stability analyses, TGAs were carried out in a TA Instrument Simultaneous SDTQ600, New Castle, DE, USA, which allows DSC-TGA measurements up to 1500 °C and has a balance sensitivity of 0.1 μg. The analyses were performed in under a 50 mL/min air atmosphere to simulate real boundary conditions. The heating rate used to perform the PCM decomposition tests was 10 °C/min from 40 to 600 °C, and the opened 100 μL alumina crucibles were filled with around 1/3 volume of material leading to average sample masses of around 22 mg, depending on the density of each material.

3.3. Cycling Stability

The cycling stability is studied to detect changes in the thermophysical and chemical properties of the PCM after a certain number of melting and freezing cycles. In this study, the cycling stability tests were divided in two steps. First, the sixteen PCMs were subjected to complete cycling tests during 100 cycles. Once the PCM underwent the required number of cycles, the thermophysical and chemical properties were evaluated. Notice that based on previous experiences, the cycling stability changes normally start during the first thermal cycles due to thermal degradation or after many cycles due to thermal stress.

The cycling tests were performed using a Venticell oven (Comfort line) from the MMM Group, Munich, Germany, with the air flap lever closed. Due to the fact that in the present study the authors wanted to simulate real operating conditions, samples of 150 ± 20 g of the sixteen PCMs were closed with aluminium foil in a glass recipient. This means that the materials were in contact with air during all the tests. Two separate cycling tests were designed, according to the melting temperature reviewed in the literature, to avoid degradation at higher temperatures and to ensure the entire phase change transition during the cycling procedure. The first cycling test identified the PCMs with phase change temperatures between 120 and 150 °C: sebacic acid, HDPE, benzoic acid, phtalic anhydride, urea, benzamide, maleic acid, and dimethyl terephthalate. The second cycling test identified the PCMs with phase change temperatures between 150 and 200 °C: adipic acid, DMPA, D-mannitol, benzanilide, potassium thiocynate, dulcitol, hydroquinone, and salycilic acid. A dynamic cycling method was established for both tests at a constant heating and cooling rate of 3.2 °C/min.

In order to evaluate the cycling stability and quantify the variation of the thermophysical and chemical properties of all the PCMs, three different measurement points were established:

- Measurement 1: 0 cycle;
- Measurement 2: 10th cycle;
- Measurement 3: 100th cycle.

The thermophysical properties studied in this paper were the phase change temperature and phase change enthalpy. These properties were evaluated using a DSC 822e from Mettler Toledo, Columbus, OH, USA, under a nitrogen atmosphere, which has an uncertainty of ±0.1 °C for temperatures and ±3 kJ/kg for enthalpies. The methodology followed a two-cycle program. A first melting and solidification cycle at 10 °C/min rate was performed to ensure good contact with the crucible base. The second cycle was performed at 0.5 °C/min rate, and the mean values of temperature and enthalpy were calculated. Two temperature ranges were evaluated following the same criteria used in the cycling tests, i.e., a temperature program which ranged from 90 to 150 °C for the PCM with a melting temperature lower than 150 °C and a temperature program which ranged from 150 to 200 °C for the remaining PCMs. Three samples of each material which were placed in 40 μL aluminum crucibles (maximum filled with two thirds of their volume, with an average sample mass of 10 mg, to avoid oxidation and taking into account volume expansion), were analysed to ensure repeatability of the tests.

The chemical characterization was carried out using a Fourier transform infrared (FT-IR) spectroscopy with attenuated total reflectance (ATR), which analyses the PCM chemical degradation caused by thermal cycling. The advantage of ATR is the possibility of obtaining the spectra directly from the sample, without any specific sample preparation. The partial or total disappearance of the characteristic peaks and/or the appearance of new peaks can indicate that the material is being oxidized or degraded. This analysis was carried out with a Spectrum Two™ from Perkin Elmer, Waltham, MA, USA. It allows analysing substances in solid and liquid states. It was optimized by a wavelength range between 4000 and 350 cm^{-1}, and its standard spectral resolution is 0.5 cm^{-1} accounting for four infrared scans for each analysis; the data recorded are their means. Its functionality is based on the characteristic wave numbers at which the molecules vibrate in infrared frequencies.

4. Results

4.1. Health Hazard

Table 3 shows the health hazard rating from both the NFPA 704 standard and GHS statements of the materials under study. As explained above, the NFPA 704 standard rates the relationship between hazard and exposure, while the GHS specifies the damages that the material can cause.

Table 3. Safety and health hazard information of the PCMs under study [15,16].

Material	NFPA 704	GHS Statement
HDPE	0	This material is not hazardous
Sebacic acid	1	Causes skin irritation Causes serious eye irritation May cause respiratory irritation
Dimethyl terephthalate	1	May cause an allergic skin reaction
D-mannitol	1	Hazardous in case of ingestion. Slightly hazardous in case of skin contact (irritant), of eye contact (irritant) or inhalation
Adipic acid	1	Causes serious eye irritation
Benzanilide	1	Harmful if swallowed May cause respiratory irritation Causes skin irritation Causes serious eye irritation
Dulcitol	1	Hazardous in case of ingestion. Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation *
Benzoic acid	2	Harmful if swallowed May cause respiratory irritation Causes skin irritation Causes serious eye irritation Causes damage to organs through prolonged or repeated exposure Causes serious eye damage
Benzamide	2	Harmful if swallowed Suspected of causing genetic defects
Urea	2	May cause respiratory irritation Causes skin irritation Suspected of causing cancer May cause damage to organs Causes serious eye irritation
Salycilic acid	2	Toxic if swallowed Causes serious eye irritation
Hydroquinnone	2	Harmful if swallowed Harmful in contact with skin Suspected of causing genetic defects Suspected of causing cancer Causes serious eye damage May cause an allergic skin reaction
Phtalic anhydride	3	Harmful if swallowed May cause respiratory irritation Causes skin irritation May cause an allergic skin reaction Causes serious eye damage May cause allergy or asthma symptoms or breathing difficulties if inhaled
Maleic acid	3	Harmful if swallowed Harmful in contact with skin May cause respiratory irritation Causes skin irritation Causes serious eye irritation May cause an allergic skin reaction
Potassium thiocynate	3	Harmful if swallowed Harmful in contact with skin Harmful if inhaled Causes serious eye irritation
DMPA	**	Causes serious eye irritation May cause respiratory irritation

* The toxicological properties of this substance have not been fully investigated. ** NFPA 704 health hazard division (blue) has not been found in the literature.

A wide variety of health hazards ranging from 0 to 3 is observed. Among the sixteen materials which were evaluated, HDPE showed the lowest health hazard value in the NFPA 704 standard, meaning that it is non-hazardous under any condition. Six other materials showed a health hazard rate of 1. According to the GHS statement, these materials may cause irritation or can be hazardous at long exposure. Therefore, they are also suitable for selection but safety measures should be taken into account when using them [8]. The other eight materials present higher values in the NFPA 704 standard and are suggested to be discarded. Nonetheless, if a specific application requires the use of any of these materials, the use of the established safety measures is compulsory to avoid serious damages.

4.2. Thermal Stability

Table 4 shows the maximum thermal-stable temperature and final degradation temperature of the PCMs under study, which are ordered by their maximum thermal-stable temperature.

Notice that there are only five PCMs, potassium thiocynate, HDPE, dulcitol, adipic acid, and D-mannitol, with a maximum thermal-stable temperature of 200 °C or higher. The most stable material over this temperature is potassium thiocynate, which presents 540 °C as a maximum thermal-stable temperature, followed by HDPE and dulcitol with 309 °C and 293 °C, respectively. Moreover, there are two additional PCMs, benzanilide and DMPA, which have a maximum thermal-stable temperature within the upper limit of the requested operating temperatures, and therefore they could be considered to be suitable for thermal processes within the temperature range of 120–200 °C without degradation. On the other hand, there are two materials, benzoic acid and sebacic acid, whose maximum thermal-stable temperature is 121 °C or lower and therefore should be discarded for the operation in this temperature range. Finally, there are seven other PCMs, hydroquinone, urea, maleic acid, benzamide, salycilic acid, phtalic anhydride, and dimethyl terephtalate, whose suitability within this temperature range will strongly depend on the operating conditions (heat source temperature) of the thermal process for which they are planned to be implemented. However, it should be made clear that the TGAs were performed assuming the worst-case scenario, which is air continuously flowing around the material, but in real thermal applications, it is difficult to achieve such disadvantageous conditions.

Notice that there are six PCMs, benzoic acid, sebacic acid, phtalic anhydride, dimethyl terephthalate, hydroquinone, and salycilic acid, which start the degradation before or during the phase change. The reason lies in the fact that TGAs were performed by applying a constant 50 mL/min air flow to an open crucible. Therefore, the thermal degradation conditions were not exactly the same as those used for thermal cycling of the sample under study.

Table 4. Maximum thermal-stable temperature, final degradation temperature of the PCMs under study.

Material	Maximum Thermal-Stable Temperature (°C)	Final Degradation Temperature (°C)
Potassium thiocynate	540	>600
HDPE	309	540
Dulcitol	293	481
D-mannitol	259	424
Adipic acid	203	379
Benzanilide	196	315
DMPA	190	431
Hydroquinone	157	240
Urea	148	500
Maleic acid	141	212
Benzamide	138	225
Salycilic acid	133	203
Phtalic anhydride	129	210
Dimethyl terephthalate	128	265
Benzoic acid	121	195
Sebacic acid	118	201

4.3. Cycling Stability

In this section, the variation of the thermophysical properties (phase change temperatures and enthalpies) and the variation of the chemical properties of the studied PCM are presented. In this section, only the most representative results are shown for a better comprehension.

4.3.1. Thermophysical Characterization (Phase Change Temperature and Enthalpy)

DSC results show that four out of the sixteen evaluated PCMs did not show solidification under described conditions during the first cycle and, as a consequence, they cannot be considered for latent heat TES purposes. These PCMs are maleic acid, DMPA, salicylic acid, and urea. Hence, from a thermosphysical characterization point of view, only twelve out of the sixteen materials can be considered for latent heat storage unit purposes. Errors of 10% for melting enthalpy and 5% for melting temperature are stated as acceptable for the DSC measurements and are represented in the graphics with error bars [17].

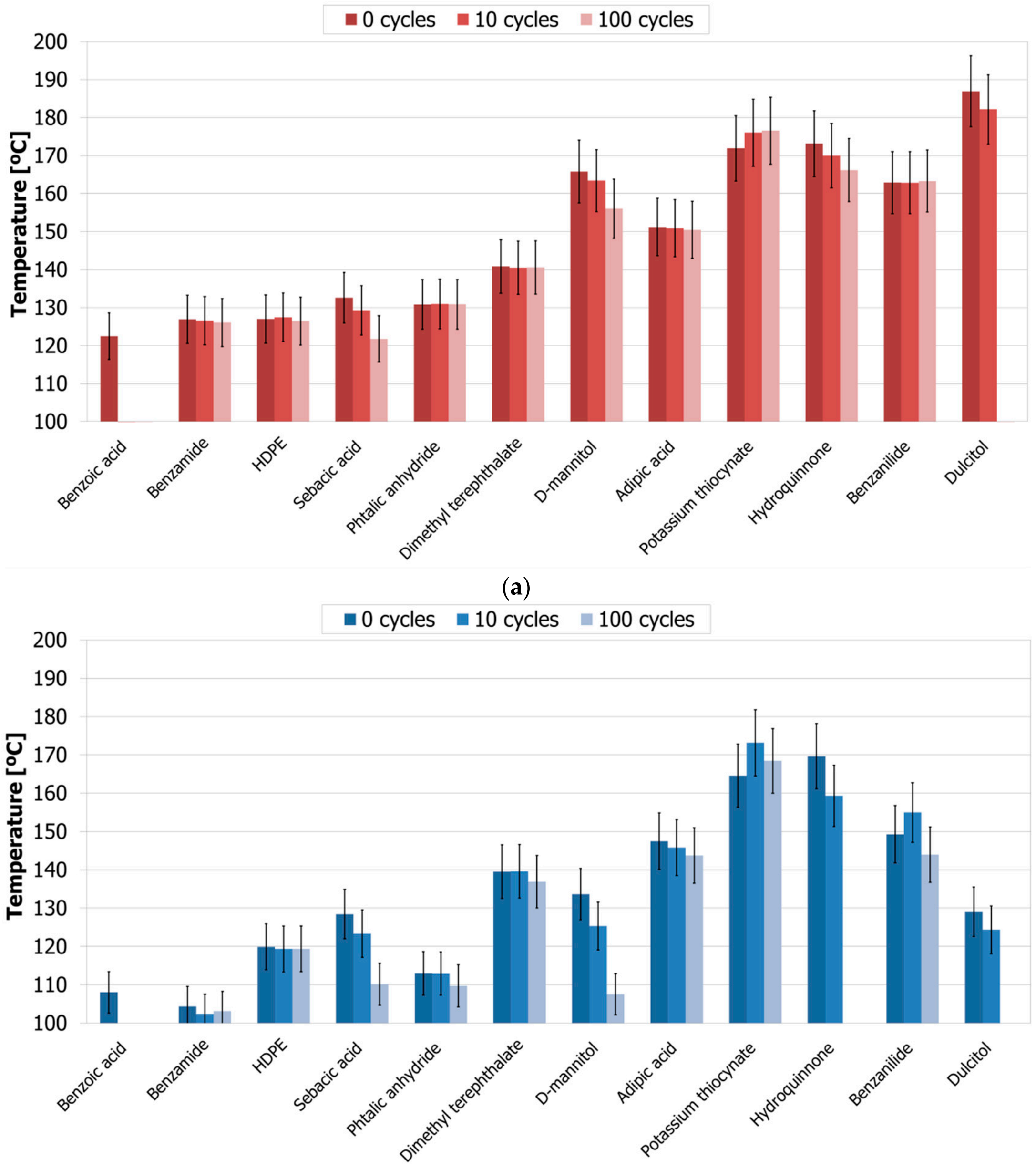
Figure 1 shows the evolution of the phase change temperature (melting Figure 1a and solidification Figure 1b) of the twelve PCMs which presented suitable thermal results at the initial stages of the thermosphysical characterization after 0, 10 and 100 cycles. It is important to highlight that at the zero cycle, some PCMs showed remarkable differences between melting and solidification temperatures, like benzamide, benzanilide, D-mannitol, and dulcitol. After 10 cycles, benzoic acid did not show phase change under analysis conditions, and the remaining materials presented variations lower than 6.5%., i.e., D-mannitol and hydroquinone, which had a higher variation in the solidification temperature, with values of 6.2% and 6.1%, respectively. After 100 cycles, dulcitol and hydroquinone did not show phase changes under analysis conditions. Moreover, sebacic acid and D-mannitol showed a decrease in their phase change temperatures in comparison to their initial values, especially at the solidification temperature, with values of 14.3% and 19.5%, respectively. Hence, from the D-mannitol and sebacic acid results, it can be seen that the modification in the phase change temperature and latent heat with increasing number of cycles is noteworthy (more than 20% in the case of latent heat). On the other hand, the thermophysical properties of benzamide, HDPE, dimethyl terephthalate, adipic acid, potassium thiocynate, and benzanilide remained almost constant during all cycling tests. However, after 100 cycles D-mannitol, benzamide and benzanilide showed important temperature differences between solidification and melting processes.

The evolution of the melting and solidification enthalpies after 0, 10 and 100 cycles of the twelve PCMs, which presented suitable results at the initial stages of the thermophysical characterization, is presented in Figure 2a,b, respectively. At the initial stage, a wide range of enthalpies values were observed, from a minimum value of 100–120 kJ/kg for benzoic acid, to values up to 400 kJ/kg for dulcitol. The remaining PCMs showed phase change enthalpies that ranged between 120 and 280 kJ/kg. Results after 100 cycles showed that melting enthalpies of benzamide, HDPE, dimethyl terphthalate, adipic acid, potassium thiocynate, phtalic anhydride and benzanilide presented variations lower than 15%.

From the phase change temperature and enthalpy point of view, six PCMs, benzamide, HDPE, dimethyl terphthalate, adipic acid, potassium thiocynate, phtalic anhydride and benzanilide, presented values which were suitable for partial load operation conditions in latent heat TES systems. The variations in these parameters observed along thermal cycles might be due to the degradation of the chemical structure of the PCMs with increasing number of cycles [18]. Hence, the material could not form the first crystal during the solidification process of the thermal cycling, and hysteresis phenomena took place. Throughout a considerable number of phase change transition processes, new compounds were formed, which may have different latent heat than that of the fresh PCMs. In order to deeply analyse the described phenomena, infrared (FT-IR) spectroscopy was carried out.

4.3.2. Chemical Characterization

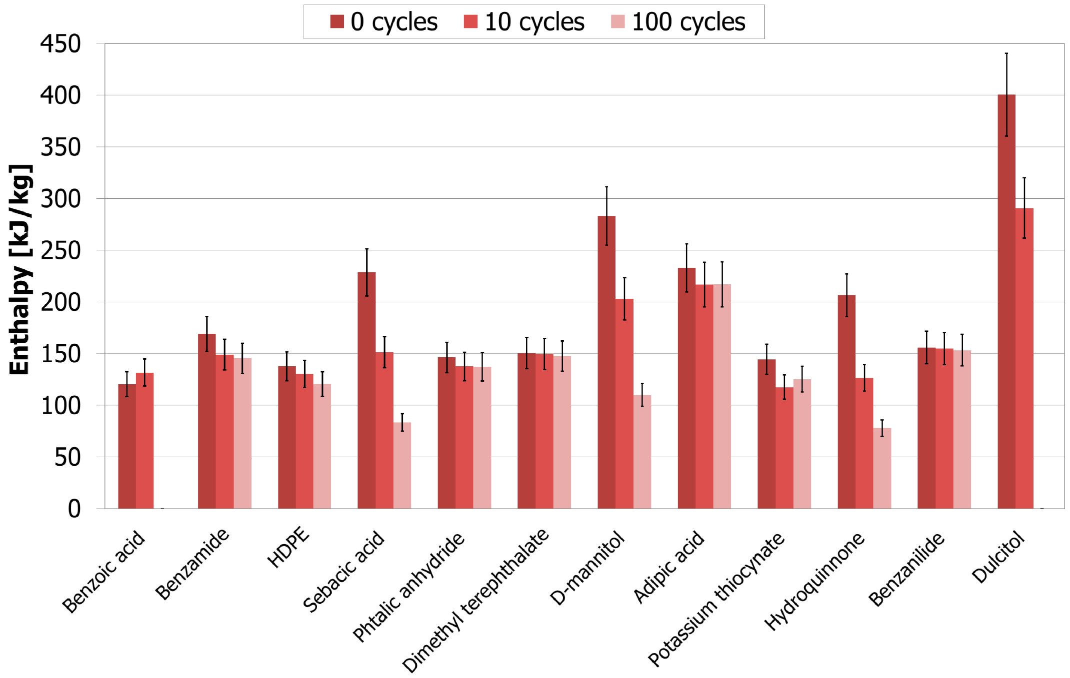
In order to simplify the analysis for chemical degradation, two peaks of each material were considered as characteristic peaks. The first peak considered was contained in the region known as the fingerprint region (1500 to 500 cm^{-1}), and the second peak was contained in the high-wavenumber region (4000 to 1500 cm^{-1}).



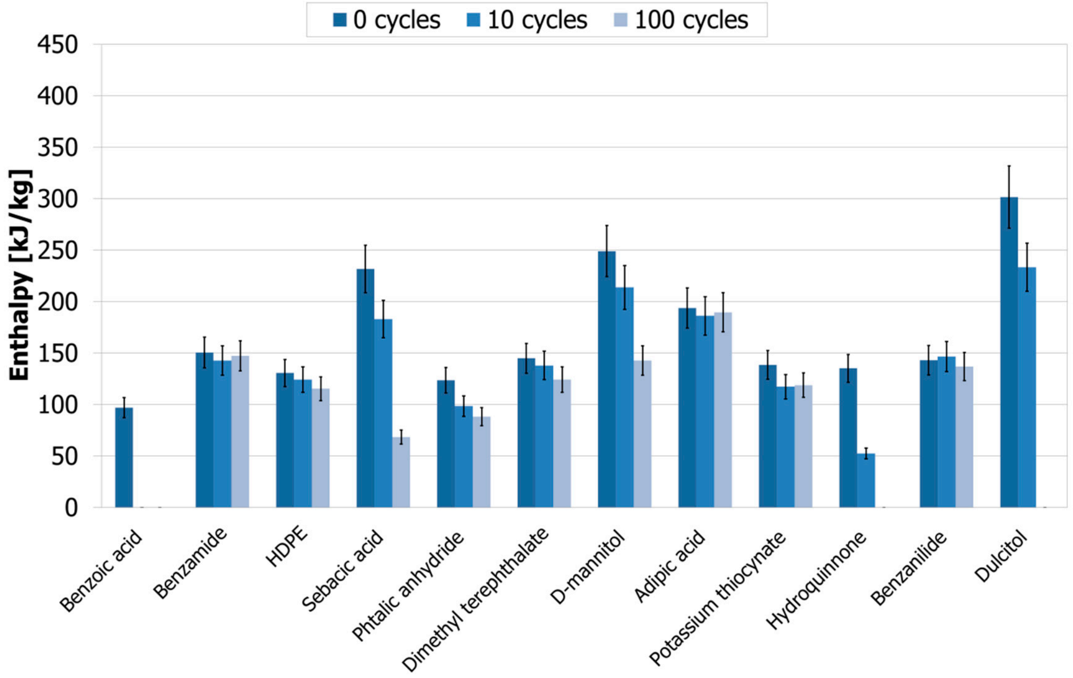
(**a**)

(**b**)

Figure 1. Phase change temperature: (**a**) melting; (**b**) solidification.



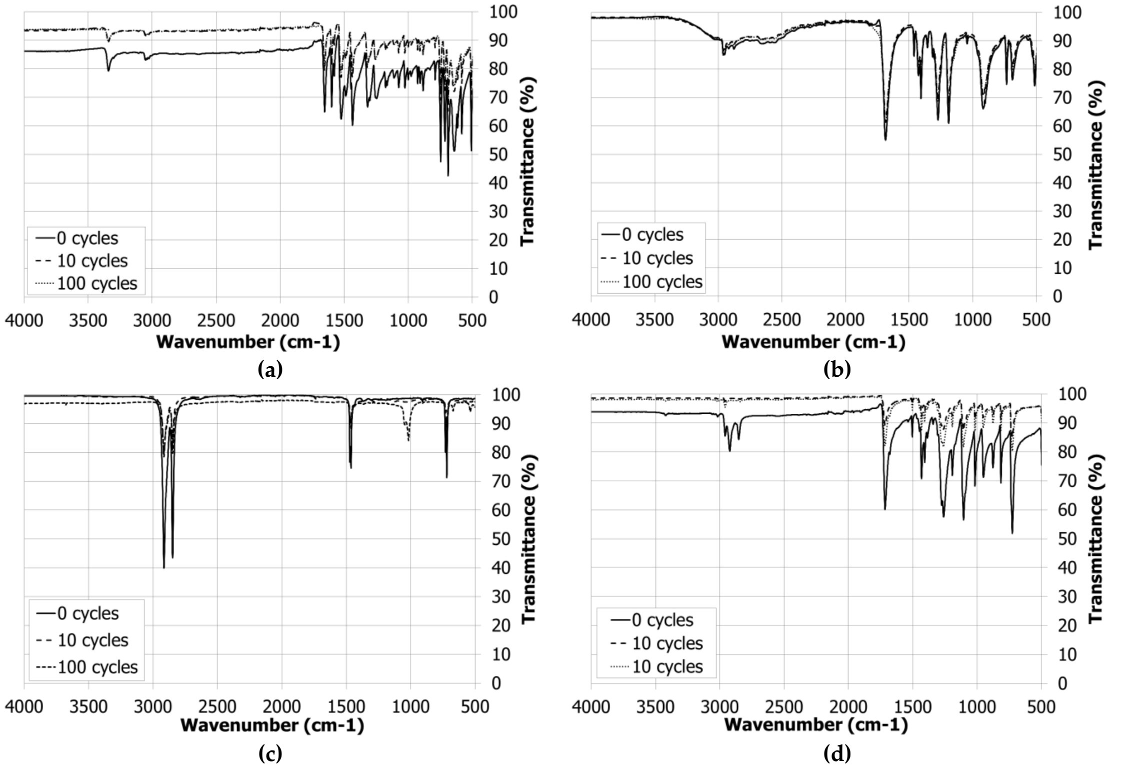
(**a**)



(**b**)

Figure 2. Phase change enthalpy: (**a**) melting; (**b**) solidification.

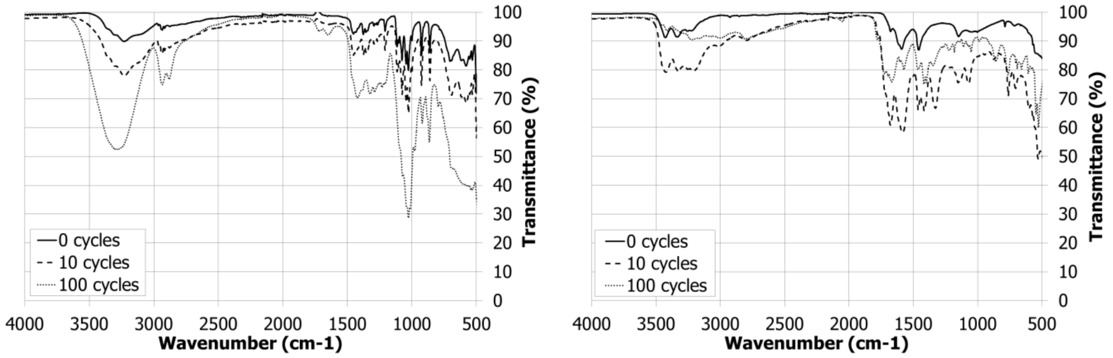
The chemical characterization showed that the results obtained could be classified into three different groups and, for a better comprehension, two examples of each are shown in Figure 3. The first group contained the PCMs which presented no chemical degradation over cycles since the FT-IR spectrums were practically equal and the two considered peaks remained identical. Among the sixteen PCM evaluated, it was found that adipic acid (see Figure 3a) and benzanilide (see Figure 3b) showed this behaviour. The second group contained the PCMs which experienced a certain level of degradation since differences between initial and cycled FT-IR spectra existed. It was observed that HDPE (see Figure 3c), dimethyl terephthalate (see Figure 3d), hydroquinnone, potassium thiocyanate, benzamide, phtalic anhydride, and sebacic acid, presented slight variations in their spectrum. The high-wavenumber region-peak of dimethyl terephthalate (2853 cm^{-1}), hydroquinnone (3015 cm^{-1}), and potassium thiocyanate (3432 cm^{-1}) did not appear after thermal cycling. Although benzamide basically did not present differences in its spectrum after 10 thermal cycles, several chemical degradation processes took place after 100 cycles. In this case, peaks from both regions were moved to higher transmittance values (768 and 3363 cm^{-1}). Phtalic anhydride peaks remained at the same wavenumber after cycling (903 and 1758 cm^{-1}), although transmittance values shifted during thermal cycling. Sebacic acid showed a similar behaviour and both considered peaks (923 and 1687 cm^{-1}) did not change, but the spectrum shifted to lower transmittance values. The HDPE spectrum presented two sharp peaks in the high wavenumber region, corresponding to CH_2 asymmetric stretching (approx. 2919 and 2851 cm^{-1}). The characteristic HDPE doublet observed in the fingerprint region (1473 and 1463 cm^{-1}, bending deformation) appeared slightly displaced after thermal cycling. In the HDPE spectrum, it is also important to notice that after 100 cycles, a new peak appeared at 1019 cm^{-1}, indicating the formation of new bonds between polymer chains (attributed to C–O bond stretching). Finally, the third group contained the PCMs which underwent serious chemical degradation since huge differences in the FT-IR spectra of cycled materials could be noticed. It was found that dulcitol (see Figure 3e), urea (see Figure 3f), salycilic acid, D-mannitol, maleic acid, and benzoic acid showed this behaviour. New peaks appeared in the spectra of urea (1334, 1411 and 1069 cm^{-1}) and salycilic acid (1739 cm^{-1}). D-mannitol presented displaced peaks in the high wavenumber region, and several peaks at low wavenumbers disappeared (i.e., 575 cm^{-1}). After 100 cycles, the fingerprint region peaks of maleic acid and benzoic acid presented profound differences (861 and 931 cm^{-1} respectively). Dulcitol showed that in the fingerprint region, few peaks disappeared (500 to 800 cm^{-1} region), while in the high-wavenumber region, large differences were observed. In addition, new peaks appeared in the cycled samples in the 1640 and 1740 cm^{-1} region (CO-double bonds), which was an indication of oxidation during cycling.



(a) (b)

(c) (d)

Figure 3. *Cont.*



(e) (f)

Figure 3. FT-IR spectroscopy results: (**a**) Adipic acid; (**b**) Benzanilide; (**c**) HDPE; (**d**) Dimethyl terephthalate; (**e**) Dulcitol; (**f**) Urea.

5. General Discussion

Taking into account the thermophysical characterization from the cycling stability tests results, only dimethyl terephthalate, benzanilide, potassium thiocyanate, HDPE, benzamide, phtalic anhydride, and adipic acid showed a suitable stability after 100 cycles. However, benzamide and benzanilide presented remarkable differences between solidification and melting temperatures at the laboratory scale. Therefore, these two candidates might be interesting to be tested at a higher scale to study this phenomenon since the differences between solidification and melting temperatures and subcooling of PCM are mass dependent [17]. From this first filter, and taking into account the chemical characterization, it was seen that adipic acid showed the same chemical spectrum after cycling tests, while HDPE, potassium thiocyanate, and dimethyl terephthalate did not exhibit important chemical degradation but rather the appearance or disappearance of some peaks. Moreover, from the health hazard point of view, potassium thiocynate should be disregarded due to its high hazard value according to the methodology explained. Adipic acid and dimethyl terephthalate present a low health hazard value, whereas HDPE appears to be hazardless, being easy to handle and not presenting any hazardous GHS statement. Finally, bearing in mind the thermal stability tests, only HDPE and adipic acid would be suitable PCMs for thermal processes working under partial load operating conditions in the temperature range between 120 and 200 °C.

A summary of the results of the deep experimental characterization of the sixteen PCM in the temperature range between 120 and 200 °C is provided in Table 5.

Table 5. Summary of the characterization of the sixteen PCMs under study.

Material	Health Hazard	Cycling Stability (after 100 Cycles)		Thermal Stability	Suitable Material for Partial Load Applications
		Phase Change Enthalpy Loss (%)	Chemical Degradation [a]	Maximum Thermal-Stable Temperature	
Benzoic acid	2	100	++	121	No
Benzamide	2	14	++	138	No
High density polyethylene (HDPE)	0	12	+	309	Yes
Sebacic acid	1	63	++	118	No
Phtalic anhydride	3	6	+	129	No
Maleic acid	3	**	++	141	No
Urea	2	**	++	148	No
Dimethyl terephthalate	1	2	+	128	No
D-mannitol	1	61	++	259	No
Adipic acid	1	7	-	203	Yes

Table 5. *Cont.*

Material	Health Hazard	Cycling Stability (after 100 Cycles)		Thermal Stability	Suitable Material for Partial Load Applications
		Phase Change Enthalpy Loss (%)	Chemical Degradation [a]	Maximum Thermal-Stable Temperature	
Salycilic acid	2	**	++	133	No
Potassium thiocynate	3	13	+	540	No
Hydroquinnone	2	62	++	157	No
Benzanilide	1	2 ***	-	196	No
Dulcitol	1	100	++	293	No
2,2-Bis(hydroxymethyl) propionic acid (DMPA)	*	**	++	190	No

[a] Chemical degradation: - no degradation; + no remarkable degradation; ++ remarkable degradation. * NFPA 704 health hazard division (blue) has not been found in the literature. ** The material does not show phase change under analysis conditions. *** The material presents remarkable differences between solidification and melting temperatures at the laboratory scale.

6. Conclusions

The selection of a PCM to be implemented in thermal processes working under partial load operating conditions in a temperature range between 120 and 200 °C was successfully performed. Sixteen PCMs were preselected for this study. The selection procedure followed a methodology which studied the health hazard, cycling stability and thermal stability of the PCMs in the mentioned range. In this study, the cycling stability tests were performed at a higher sample mass (150 ± 20 g) than in previous studies and under real atmospheric conditions which can hinder the PCM performance in some cases due to oxygen presence [11].

Considering the results obtained, adipic acid and high-density polyethylene (HDPE) are suitable options. They do not present loses of more than 12% of their thermal storage capacity after 100 cycles, do not show significant changes in the chemical structure and presents low hazardous values, and their degradation starts at temperatures higher than 200 °C.

Commodity polymers such as HDPE are cheap plastics to produce. In an industrial application, price is proved to be one of the most important aspects in the material selection process [10]. Based on price and health hazard, HDPE is the material selected for application between 120 and 200 °C. Further research on different partial loads profiles at a pilot plant scale implementing HDPE will be performed.

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