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Thermal analysis of phase change materials in the temperature range 120–150 °C

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ABSTRACT

Latent heat storage systems, using phase change materials (PCMs), present the advantage of a high storage density at nearly constant temperature. They offer intrinsic advantages for heat storage in combination with steam as heat transfer fluid. Important applications of these storage systems are the areas of solar industrial process heat supply and heat recovery in industrial batch processes.

The presented work aims to identify the most suitable PCMs, according to the studied temperature range (120–150 °C) and is based both on literature review and thermal analysis measurements. The thermal behaviour of eleven potential storage materials was studied by means of thermogravimetry (TG) and differential scanning calorimetry analysis (DSC), coupled with a quadrupole mass spectrometer (QMS). The paper emphasizes the importance of the measurement conditions on the results. In particular the impacts of the type of crucible (open/closed), the atmosphere (N_2, N_2/O_2) and the cycling stability are presented.

1. Introduction

The storage of thermal energy is both environmentally and economically vital. It is the key to bridging the time gap between the thermal energy supply and the energy demand. In the industry, the demand for heat is important, for example the annual demand for Germany can be estimated at 120 TWh in the temperature range of 100–400 °C [1]. Among this demand, a large part is used to produce steam. The development of storage systems would allow producing a part of this industrial steam efficiently and sustainably, using solar and/or the recovery of waste heat.

Thermal energy storage is based on three major concepts, namely: sensible and latent heat, as well as thermo-chemical storage [2]. The present paper considers the latent heat storage concept. This technology has been extensively studied for low temperature application, up to 100 °C [3–8]. Less studied is the temperature regime above 120 °C especially for the process heat sector and solar power generation.

This paper is directed towards the selection of PCMs for the temperature range 120–150 °C. PCMs are classified into two major groups, namely organic and inorganic materials. It has been chosen to focus on organic materials which are less studied and more common in this temperature range compared to inorganic anhydrous salts. In open literature, detailed studied of few examined PCMs have been done (urea, high density polyethylene). However, most PCM literature in this temperature range presents a long list of PCMs with limited measurements [9–14]. Furthermore, data presented are provided by different authors, giving rise to varying experimental conditions. This makes it difficult to compare the candidate PCMs.

To fulfil our objective, the selection of the most appropriate PCM in the temperature range 120–150 °C, a methodology was developed. The first step of our study was an extended literature review. The second step was to select, among all the listed PCMs, the potentially most promising materials. The third step was to analyse these materials by thermogravimetry (TG) and differential scanning calorimetry (DSC), coupled with quadrupole mass spectrometry (QMS) gas analysis.

2. Materials screening

The overall objective of this study is to determine new organic phase change materials (PCMs) to store thermal energy in a temperature range from 120 to 150 °C. In order to reach this objective, a preliminary selection, presented in Table 1, has been first performed. It allowed us to obtain organic PCMs mainly considered in the open literature [9–14].

In order to select the most promising candidates, the following criteria have been defined:

- low toxicology and ecological impact;
- economics (based on a laboratory supply price);
- weakly hygroscopic.

The application of these criteria to all materials listed in Table 1 allows us to reduce our study to the following PCMs:

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Nomenclature

CAS	chemical abstracts service number
LD50	lethal dose 50, mg kg^{-1}
L	latent heat, J g^{-1}
MSDS	material safety data sheet
n.a.	not available
T	temperature, °C
Greek symbol	
ρ	density, kg m^{-3}
Subscripts	
bp	boiling point
fp	flash point
mp	melting point
on	onset
sub	sublimation
tr	solid–solid transition

- two solid–solid materials: trometanol and dimethylpropionic acid;
- three dicarboxylic acids: sebacic acid, adipic acid and maleic acid;
- one sugar, glucose-D;
- one polymeric hydrocarbon, high-density polyethylene;
- three aromatic hydrocarbons: benzoic acid, phthalic anhydride, dimethyl terephthalate;
- and finally, urea.

To determine the main characteristics of these potential storage materials a calorimetric study has been performed. Analysis methods and results are outlined in Sections 3 and 4, respectively. A literature review of the listed candidate PCMs has been performed before starting the measurement and in the following this review is presented.

2.1. Solid–solid transition materials

Some materials exposed to an input of thermal energy present a transition (with a large enthalpy) without a solid–liquid phase change. When this transition occurs in the solid phase, these materials are referred to as solid–solid transition materials (SSTMs). Such materials present some advantages such as a small volume change at the transition (e.g., 5%), no leakage and no phase separation [15].

Trometanol, tris(hydroxymethyl)aminomethane (TAM) or 2-amino-2-(hydroxymethyl)propane-1,3-diol, with the brut formula $C_4H_{11}NO_3$, is a colourless weakly toxic crystalline powder (LD50 = 5900 mg kg^{-1}). It is slightly soluble in water and in alcohol but sparingly soluble or insoluble in hydrocarbons [16]. Trometanol is used as buffer or adjuvant in many pharmaceutical preparations. It is also used for modifying resins, drying oils and as an emulsifier [17].

In the area of thermal energy storage, most of the research performed on this material focuses on thermal properties of binary SSTM mixtures [18–21], for example trometanol mixed with neopentylglycol. Results show a decrease of the transition temperature compared to the simple MTSS but also a decrease of the transition enthalpy. For example, pure TAM exhibited a respective transition temperature and enthalpy equal to 132.4 °C and 295 J g^{-1}, whereas the same compound mixed with 38% neopentylglycol presents a transition at 35.6 °C and the corresponding enthalpy is equals to 27.1 J g^{-1} [21].

Dimethylpropionic acid is also called 2,2-bis (hydroxymethyl) propionic acid or DMPA and its formula is $C_5H_{10}O_4$. Work in the field of thermal energy storage is limited, however, Waschull et al. [14], point out a high transition enthalpy (289 J g^{-1} at 152 °C).

2.2. Dicarboxylic acids

Aliphatic dicarboxylic acids are, at room temperature, colourless and odourless crystalline substances which can be described by the general formula HOOC–$(CH_2)_n$–COOH. Density and dissociation constant decrease with increasing chain lengths. By contrast, melting point and water solubility alternate [22].

Dicarboxylic acids are found in nature, both as free acids and as salts, however industrial processes are employed for manufacturing these compounds. They are important feedstock in the manufacture of polyamides, di- and polyesters. In addition, they are used as intermediates in many organic syntheses [23].

Sebacic acid, HOOC–$(CH_2)_8$–COOH, also called decanedoic acid is soluble in ethanol, esters, ketones and ethers. It is the starting material for polyester resins, lubricants, adhesives, fruit flavours, coating materials, printing inks, corrosion protection agents and coolants in the metalworking [24].

Adipic acid, hexanedioic acid, 1,4-butanedicarboxylic acid (HOOC–$(CH_2)_4$–COOH) is very soluble in methanol and ethanol as well as in water. It is stable in air under most conditions, but heating of the molten acid above 230–250 °C results in some decarboxylation to give cyclo pentanone. Adipic acid is the most important commercialized dicarboxylic acid. It appears only sparingly in nature but is manufactured worldwide on a large scale. Its primary application (80% of the production) is in the production of nylon 66 polyamide. Other miscellaneous applications are in the adhesives, insecticide, tanning and dying, and textile industries. Total worldwide annual capacity for adipic acid was 2.5×10^6 tonnes in 1999. Principal hazards concerning adipic acid are related to the dust composition which can cause skin and mucus membrane irritation. Furthermore some caution concerning the risk of explosion of fumes must be taken when large quantities are handled [25].

Maleic acid, or cis-butenedioic acid, has the molecular formula HOOC–CH=CH–COOH. It has a sour, astringent, characteristic taste, and is very soluble in water and alcohol. Maleic acid is very reactive at both its carboxyl groups and its double bond. It is stereoisomeric with fumaric acid in which it can be transferred thermally or catalytically [26]. Isomerisation occurs slowly already at temperatures as low as 100 °C [27]. Maleic acid does not occur naturally. It is used industrially for the production of polymers, synthetic resins and maleic esters. It is a component of printing inks, paints and coatings. In the household sector it can be found as a component of detergents, cleaning agents, detergents for dishwashers, toilet-cleaning products. Maleic acid is also used in drug formulations, cosmetics, toothpastes and shampoos [26].

The literature review, presented in annex 1, highlights that dicarboxylic acids have high enthalpies (>220 J g^{-1}). The thermal behaviour of dicarboxylic acids in various atmospheres has been studied by Muraishi and Suzuki [22]. The authors point out that the decomposition of sebacic, adipic and maleic acid begin at temperatures equal to 171, 181 and 146 °C in inert atmosphere and 169, 179 and 145 °C in air, respectively. Information concerning thermal cycling stability and thermal behaviour in hermetically sealed crucibles has not been found in the open literature and these aspects are examined in the present work.

2.3. D-Glucose

The word “sugar” is often used as a synonym for monosaccharides which are the most basic units of carbohydrates. The

Table 1
Overview of organic PCM with a phase change temperature comprise between 120 and 150 °C. The criteria for selecting materials are classified as positive (bold), negative but not prohibitive (italic) and crippling (strikeout). Economical criteria and MSDS data are provided from Alfa Aesar®, chemicals supplier.

System	CAS	T_{mp} (°C)	T_{bp} (°C)	T_{fp} (°C)	L ($J \cdot g^{-1}$)	ρ ($g \cdot cm^{-3}$)	MSDS*	LD50 rat ($mg \cdot kg^{-1}$)	Econom. criteria**
Solid-solid transition materials									
Trometanol (TAM)	77-86-1	132 (tr)	220	n.a.	**285**	1.35	*Xi*	5900	0
DMPA	4767-03-7	185 (tr)	n.a.	n.a.	**289**	n.a.	*Xi*	n.a.	0
Dicarboxylic acids and similars									
Sebacic acid	111-20-6	130-134	294	220	**228**	1.27	*Xi*	3400	0
Maleic acid	110-16-7	131-140	355	*127*	**235**	1.59	*Xn*	708	+
Malonic acid	141-82-2	132-136	n.a.	172	n.a.	1.62	*Xn*	1310	0
Suberic acid	505-48-6	141-144	230	210	**245**	1.02	*Xi*	n.a.	-
Adipic acid	124-04-9	151-155	256	196	**260**	1.36	*Xi*	n.a.	+
Sugars and similars									
Xylose-D	58-86-6	147-151	n.a.	n.a.	216-280	1.53	/	23000	-
~~Xylose-L~~	609-06-3	147-151	n.a.	n.a.	213	1.53	/	n.a.	~~--~~
Glucose-D	50-99-7	149-152	n.a.	n.a.	174-192	n.a.	/	25800	+
~~Fructose-D~~	3615-37-0	144-145	n.a.	n.a.	145	n.a.	/	n.a.	~~--~~
Sugar Alcohols									
~~Erythritol~~	149-35-6	120	330	n.a.	340	1.45	/	n.a.	~~--~~
Isomalt	64519-82-0	145	n.a.	n.a.	170	n.a.	n.a.	n.a.	n.a.
Maltitol	585-88-6	145-152	n.a.	n.a.	173	n.a.	/	n.a.	-
Lactitol	585-86-4	146-152	n.a.	n.a.	135-149	n.a.	n.a.	n.a.	n.a.
Polymeric hydrocarbons									
Polyethylene (HDPE)	9002-88-4	130	n.a.	287	**211-233**	0.96	/	n.a.	-
Aromatic hydrocarbons/ Arenes									
Mandelic acid	90-64-2	118-121	n.a.	n.a.	161	1.30	*Xi*	n.a.	-
Benzoic acid	65-85-0	121-123	249	128	114-147	1.08	*Xn*	1700	+
~~Picric acid~~	88-89-1	121-122	n.a.	n.a.	75	n.a.	~~T, F, E~~	n.a.	n.a.
~~trans-Stilbene~~	103-30-0	124	305	n.a.	167	0.97	~~Xn, N~~	920***	0
Benzamide	55-21-0	125-129	288	180	169	1.34	*Xn*	1125	-
Phthalic anhydride	85-44-9	131	295	152	159	1.53	*Xn*	1530	+
trans-Cinnamic acid	140-10-3	133	300	>100	153	1.25	*Xi*	100****	-
~~Phenacetin~~	62-44-2	134-137	n.a.	n.a.	137	n.a.	~~T~~	1650	0
Chlorobenzoic acid	118-91-2	140	285	153	164	1.54	*Xi*	>3200	0
Dimethyl terephthalate	120-61-6	142	288	153	170	1.29	/	>3200	+
~~4-Methylacetanilide~~	103-89-9	146-151	306	n.a.	180	n.a.	*Xn*	980***	~~--~~
Anthranilic acid	118-92-3	147	n.a.	150	148	1.41	*Xi*	4550	+
~~4-Nitroaniline~~	100-01-6	147	260	198	152	1.44	~~T~~	750	+
Others									
~~Hexacarbonyltung.~~	140-11-0	127	n.a.	n.a.	211	n.a.	~~T~~	n.a.	~~--~~
Urea	57-13-6	133-135	n.a.	n.a.	170-258	1.34	/	8471	+
~~Dimethylpyrone~~	1004-36-0	134	n.a.	n.a.	234	/	*Xn*	1670***	~~--~~

[*] Hazard Symbols: E = Explosive, F = Highly flammable, N = Dangerous for environment, T = Toxic, Xi = Irritant, Xn = Harmful
[**] Economical criteria: + = low cost, 0 = medium cost, -= high cost, -- = very high costs (based on small-scale laboratory prices)
[***] LD50 Mouse
[****] LD50 Bird

term sugar may also be applied to simple compounds containing more than one monosaccharide unit. Indeed, in everyday usage sugar signifies table sugar, which is sucrose disaccharide composed of the two monosaccharides D-glucose and D-fructose [28]. With few exceptions (e.g., deoxyribose), monosaccharides have the chemical formula $C_n(H_2O)_m$ with the chemical structure $H(CHOH)_nC{=}O(CHOH)_m$.

D-**Glucose**, or dextrose, or glucose, abbreviated D-Glc, is a colourless and odourless, sweet tasting crystalline and non-toxic compound soluble in water [29]. It occurs in many fruits and plants and also in human blood. Among 5–15 × 10^6 tonnes D-Glc is produce each year. Exposure of D-Glc and more generally carbohydrates to high temperatures leads to decomposition (dehydration) with darkening (caramelization) [28]. Our study aims at determining this decomposition temperature in different atmospheres in order to assess the potential of this storage material candidate.

2.4. High-density polyethylene (HDPE)

Polyethylene (PE) is classified according to density which is controlled by the attainable degree of crystallization and the density of the amorphous phase [30]. Densities range from 0.8 to 0.95 g cm^{-3} and are primarily determined by their underlying molecular structure which results from the way these polymers are synthesized.

High-density PE is a white opaque inert and non toxic solid. HDPE is produced by low-pressure polymerization. In the form of film, HDPE is used for example for cooking bags (frozen prepared meals, perforated bags of rice). Important applications are receptacles (cans and kegs), storage tanks, pipes (including pressure pipes up to about 1 MPa) and injection-moulded parts (e.g., crates). The world capacity for HDPE in 2006 was equal to 34 × 10^6 tonnes [30].

HDPE has been extensively studied and several times proposed as PCM in its initial form and also as form stable PCM, called crosslinked HDPE [31–34]. Takahashi reports molten polyethylene to be not stable in air, but stable in the absence of oxygen [34]. In a 500 h degradation test, sealed polyethylene showed little change in melting and crystallization temperature, as well as latent heat [35]. Our investigation aims to verify the thermal properties, such as melting range of 120–132 °C, latent heat of 180–200 J g^{-1} and thermal stability, that were previously reported.

2.5. Aromatic hydrocarbons/arenes

Benzoic acid, or benzene carboxylic acid, is a colourless and odourless monoclinic crystal. It is very soluble in methanol, alcohol and acetone. Benzoic acid is not hygroscopic and stable in air. It begins to sublime at about 100 °C. Above 220 °C it reacts with copper salts to form phenol and its derivative [36]. Decarboxylation occurs when benzoic acid is heated above 370 °C. Benzoic acid is widely distributed in nature in foliage, fruit and seeds of various plants including cherries and prunes. It is industrially produced by oxidation of toluene with air [37]. The majority of the production is used to synthesize phenol and the rest in different sectors like plasticizers, preservatives and anticorrosives, pharmaceuticals, perfumes and cosmetics. In its purest form benzoic acid is used as reference substance in DSC. The acute toxicity of benzoic acid is low. Precautions should be taken against dust during handling since it irritates the eyes and skin. Dust/air mixtures can be explosive above the flash point.

Phthalic anhydride, or isobenzofuran-1,3-dione ($C_8H_4O_3$), forms colourless needles or platelets, with a monoclinic or rhombic crystalline form. It is slightly soluble in ethanol and ether, soluble in esters, ketones, halogenated hydrocarbons and benzene [38]. As a cyclic anhydride, phthalic acid is a chemical reactive compound. The most important commercial reactions involving this compound are performed with alcohols or diols to give esters or polyesters. Phthalic anhydride is one of the technically most important aromatic compounds and is mainly produced by oxidation of O-xylene. It is an important intermediate in the production of plasticizers. In 2000, the phthalic anhydride world production capacity exceeded 4.6×10^6 tonnes [39]. The contact with phthalic acid leads to mucous membrane irritation and conjunctivitis and when prolonged may cause skin burns. Hazard data of this compound report that, in air, explosions can occur at concentrations below 100 g m^{-3}.

Dimethyl terephthalate, also known as 1,4-benzenedicarboxylic acid dimethyl ester ($C_{10}H_{10}O_4$), is almost a odourless and colourless material which is soluble in water and ethanol. Dimethyl terephthalate is a starting material for the manufacturing of polyesters with the principal use in the fiber sector. A smaller part is used as polyester resin for the production of films, coating and adhesives. The world production of this material in 1992 was equal to 12×10^6 tonnes [40]. Dimethyl terephthalate has low toxicity and cause only mild and reversible skin irritation in case of contact.

Although presented as latent heat storage materials because of their corresponding enthalpy (among 150 J g^{-1}) [12], these materials seem to have not received thermoanalytical study to validate their use.

2.6. Urea

Urea plays an important role in many biological processes. The human body produces 20–30 g of urea per day. Urea, $CO(NH_2)_2$, forms white, long, thin needles, but it can also appear in the forms of rhomboid prisms. Upon heating, urea decomposes primarily to ammonia and isocyanic. Urea is mostly used for soil fertilization but can be also used in the manufacture of urea–formaldehyde resins and melamine production. It is also used as nutrient for ruminants. In all commercial processes, urea is produced by reacting ammonia and carbon dioxide at elevated temperature and pressure. The total world production in 1997 was equal to 89×10^6 tonnes [41]. Urea has a low acute toxicity. There were no toxicological effects in rats after daily administration of 2.25 g kg^{-1} observed in the diet for one year. Urea does not show any skin or mucous membrane irritant, sensitizing, mutagenic, carcinogenic and reproductive effects [42]. Urea, as latent heat-thermal energy storage materials has been investigated by Kamimoto et al. [43]. The conclusion of this study, performed by TG and DSC measurement, is that urea is unsuitable as storage material because of its low stability. However, this material is inexpensive, non toxic and cited in the open literature [9–14]. It has been selected for our study in order to verify its thermal stability.

Table 2
Selected PCMs with CAS number, suppliers and purities.

Material	CAS	Supplier	Purity
TAM	77-86-1	Lancaster synthesis	>99%
DMPA	4767-03-7	Lancaster synthesis	>98%
Sebacic acid	111-20-6	Merck	>98%
Maleic acid	110-16-7	Merck	>99%
Adipic acid	124-04-9	Roth	>99%
Glucose-D	50-99-7	Merck	>99%
HDPE	9002-88-4	Aldrich	>99%
Benzoic acid	65-85-0	Merck	>99.9%
Phthalic anhydride	85-44-9	Merck	>98%
Dimethyl terephthalate	120-61-6	Merck	>99%
Urea	57-13-6	Roth	>99.5%

3. Thermoanalytical investigation methods

Table 2 presents the selected PCMs with the suppliers and the purities. The thermal analysis of the PCMs has been performed with a high temperature simultaneous thermogravimetry (TG) and differential scanning calorimetry apparatus, commonly called STA, model Netzsch STA449. This system allows the measurement of mass changes and thermal effects in a wide range of temperature (up to 1200 °C) and in various atmospheres. This apparatus is coupled with a quadrupole mass spectrometer (Netzsch QMS 403 C Aëolos) in order to analysis the residual gas stream. The methodology corresponding to our measurements is described below and is divided in two parts.

Purpose of the **first stage** is to record the enthalpy, onset and sublimation/decomposition temperature of each of the organic PCMs preselected. The sample initially at a constant temperature of 40 °C is subjected to a constant heat flow so that its temperature rises 10 K min^{-1} for all measurements. The final maximum temperature corresponds to the temperature to which at least 3% of the mass of the sample has evaporated or decomposed. In order to compare the results in a reliable way, the criteria T_{sub} and ΔT_{sub} are introduced. T_{sub} is defined as the temperature at which the material has lost 3% of its initial mass and ΔT_{sub} is expressed in the following equation:

$$\Delta T_{sub} = T_{sub} - T_{on} \quad (1)$$

T_{on} defines the onset temperature of the melting or solid–solid characteristic peak. In the following, T_{sub} and T_{on} are specified in Celsius, whereas the temperature difference ΔT_{sub} is defined in Kelvin. It should be noted that T_{sub} is not the decomposition temperature, because a high heating rate (10 K min^{-1}) and a high mass loss (3%) was used. Due to these boundary conditions the decomposition temperature will be artificially shifted to higher temperatures. Nevertheless, this methodology allows for a high throughput to examine several materials. In addition, the measurement conditions are clearly defined in order to compare the different materials among each other.

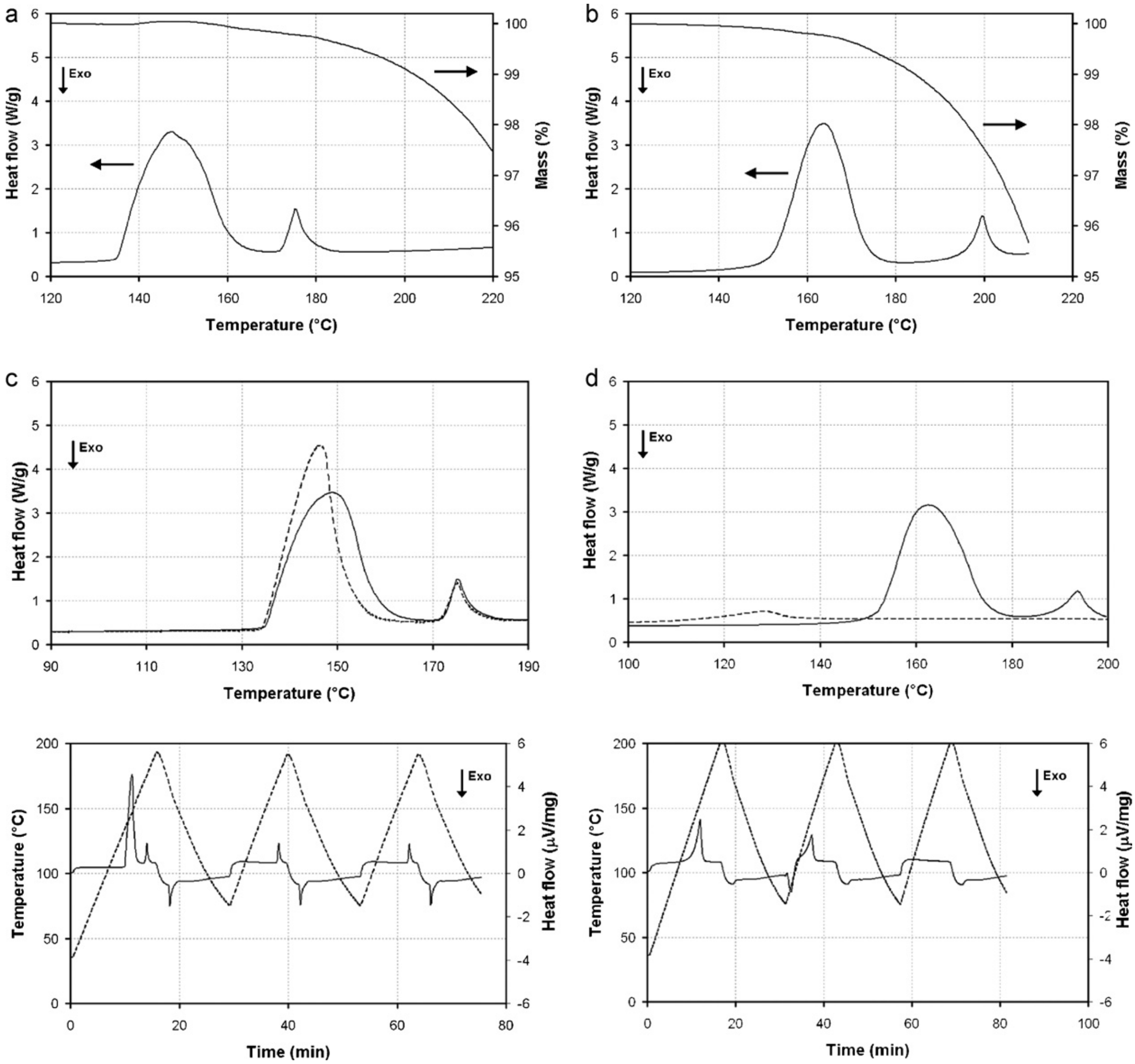

Fig. 1. Solid–solid transition materials thermal analysis measurements. First fusion cycle in open (non-hermetically sealed) crucible and nitrogen atmosphere: a) TAM; b) DMPA. Initial fifth fusion/solidification cycles: c) TAM in open (non-hermetically sealed) crucible and nitrogen atmosphere; d) DMPA in hermetically sealed crucible. Up, first fusion cycle (straight) and fifth fusion cycle (dotted); down, second, third and fourth cycle (straight), temperature program (dotted).

Some measurements showed a slight increase of the thermogravimetry signal during the melting process of the sample (see Figs. 1a and 1b, 2a and 2b, 3b, 4a and 4b). For these measurements, no assessment of this phenomenon was performed. The mass change of this peak was always smaller than 0.3% and this value is small compared to the detected mass change of 3% for the decomposition process.

At the **second stage**, stability and reliability of the fusion/solidification (or solid–solid conversion) process are studied for five cycles. The maximum temperature is 50 °C higher than the onset temperature and the temperature program performed is composed of three steps:

- A first fusion of the material performed under the conditions defined previously, allow us to know the latent heat of the sample;
- Three fusion/solidification cycles, which aim to verify the repeatability of the properties of the material and measure the characteristics of its solidification; are done with the same heating rate but without calibration;
- A final fifth fusion is performed under the same conditions as the first cycle to identify differences in the heat of fusion after cycling.

An average of 10 mg sample is needed and previous to the analysis all samples are inserted at least 30 min in a drying chamber at 120 °C. Measurements were done in various atmospheres (nitrogen, 100 mL min^{-1} and nitrogen/oxygen mixture, 80/20 mL min^{-1}) and crucibles (open aluminium crucible and hermetically sealed aluminium crucible). As a calibration material sapphire was utilized.

These different measurements are intended to estimate material behaviours in various storage system configurations:

- Thermal analysis in open crucible in nitrogen/oxygen mixture considers the behaviour of the material placed in a non-pressurized storage volume which can be in contact with the surrounding air;
- Measurements in the same crucible, but in inert atmosphere, represent a storage unit in which the material is not in contact with air but with an inert gas;

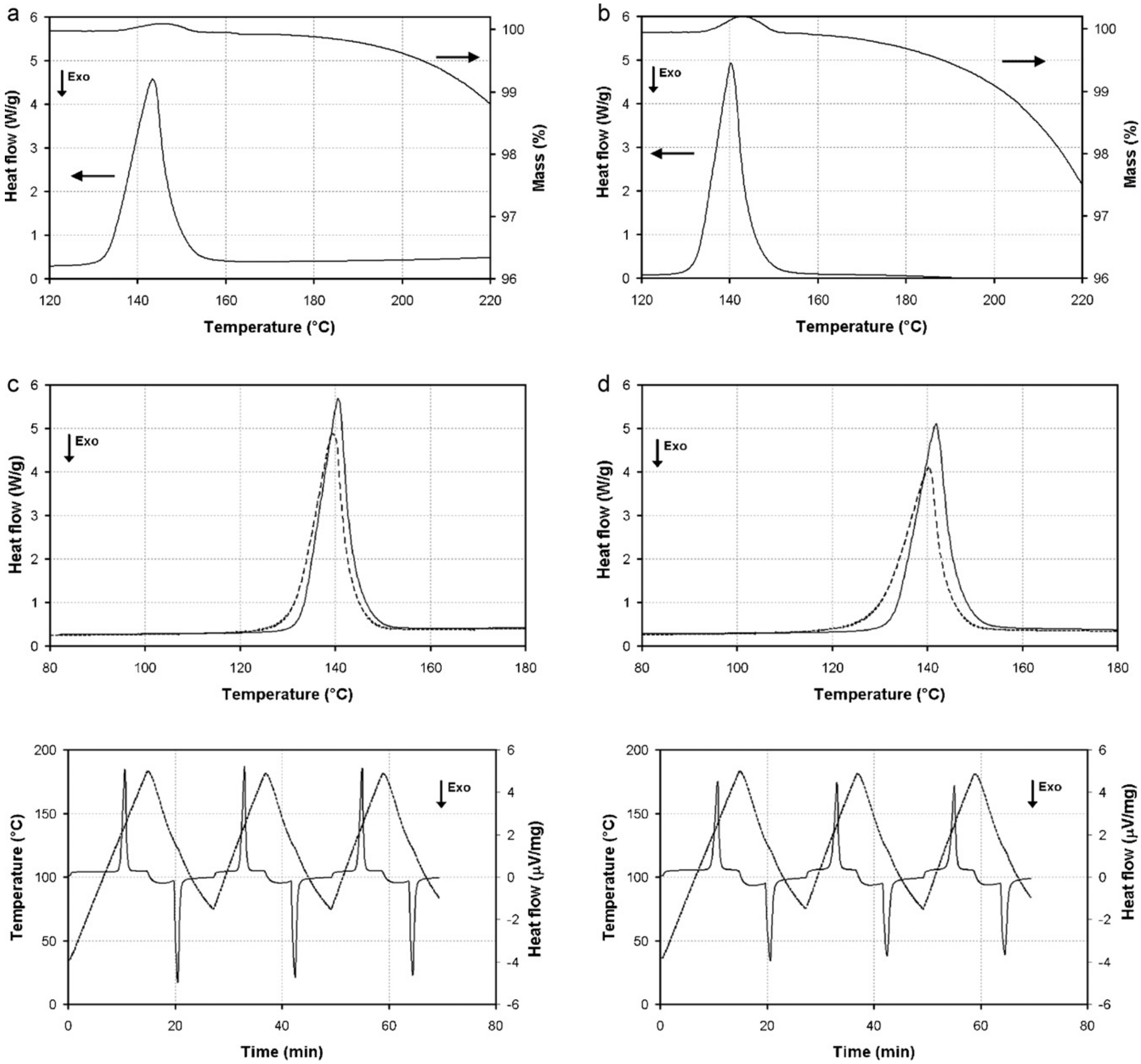

Fig. 2. Sebacic acid thermal analysis in non hermetically sealed crucible. First fusion cycle: a) in nitrogen atmosphere; b) in nitrogen/oxygen mixture atmosphere. Initial fifth fusion/solidification cycles: c) under nitrogen atmosphere; d) under nitrogen/oxygen mixture atmosphere. Up: first fusion cycle (straight) and fifth fusion cycle (dotted); down: second, third and fourth cycle (straight), temperature program (dotted).

- Then, analysis performed in hermetically sealed crucibles gives indications of the material behaviour in a closed storage tank or capsule.

4. Results and discussion

4.1. Solid–solid transition materials (SSTMs)

Fig. 1 presents thermal analysis results of trometanol (TAM, Fig. 1a) and dimethylpropionic acid (DMPA, Fig. 1b) in nitrogen atmosphere and underlines principal properties of SSTM. A first large peak linked to the solid–solid transition and a second smaller one occurring at a higher temperature related to the phase change (melting) can be observed. Concerning the TAM, the onset of the first peak is 135 °C and the related enthalpy is equal to 281 J g^{-1}. The second SSTM tested, DMPA, presents also a large storage capacity (260 J g^{-1}) at a temperature of 152 °C (20 K higher than TAM). TAM and DMPA begin to melt at 173 °C and 197 °C respectively that is to say 38 K and 45 K above their respective transition temperature. At the end of the measurement both samples are still white, this indicates that the recorded mass loss is due to sublimation and not to decomposition. Mass spectrometer measurements showed mainly water at the sublimation temperature.

The temperature at which the TAM has lost 3% of its initial mass is equal to 223 °C, hence a calculated ΔT_{sub} equals to 88 K. Similar observations for the DMPA indicate a sublimation temperature at 204 °C and this result in ΔT_{sub} equal to 52 K.

Characteristics recorded for the TAM (high latent heat and high ΔT_{sub}) show that this material could be a good storage materials in inert atmosphere. To verify this hypothesis five thermal cycles have been performed in inert atmosphere using open crucibles. Fig. 1c presents the obtained DSC-thermograms. Fig. 1c shows on the top the first fusion cycle (straight line) and the fifth cycle (dotted line). Fig. 1c also shows on the bottom the DSC-signal of the second, third and fourth melting cycle vs. time (straight line) with the temperature program vs. time (dotted line). Although a simi-

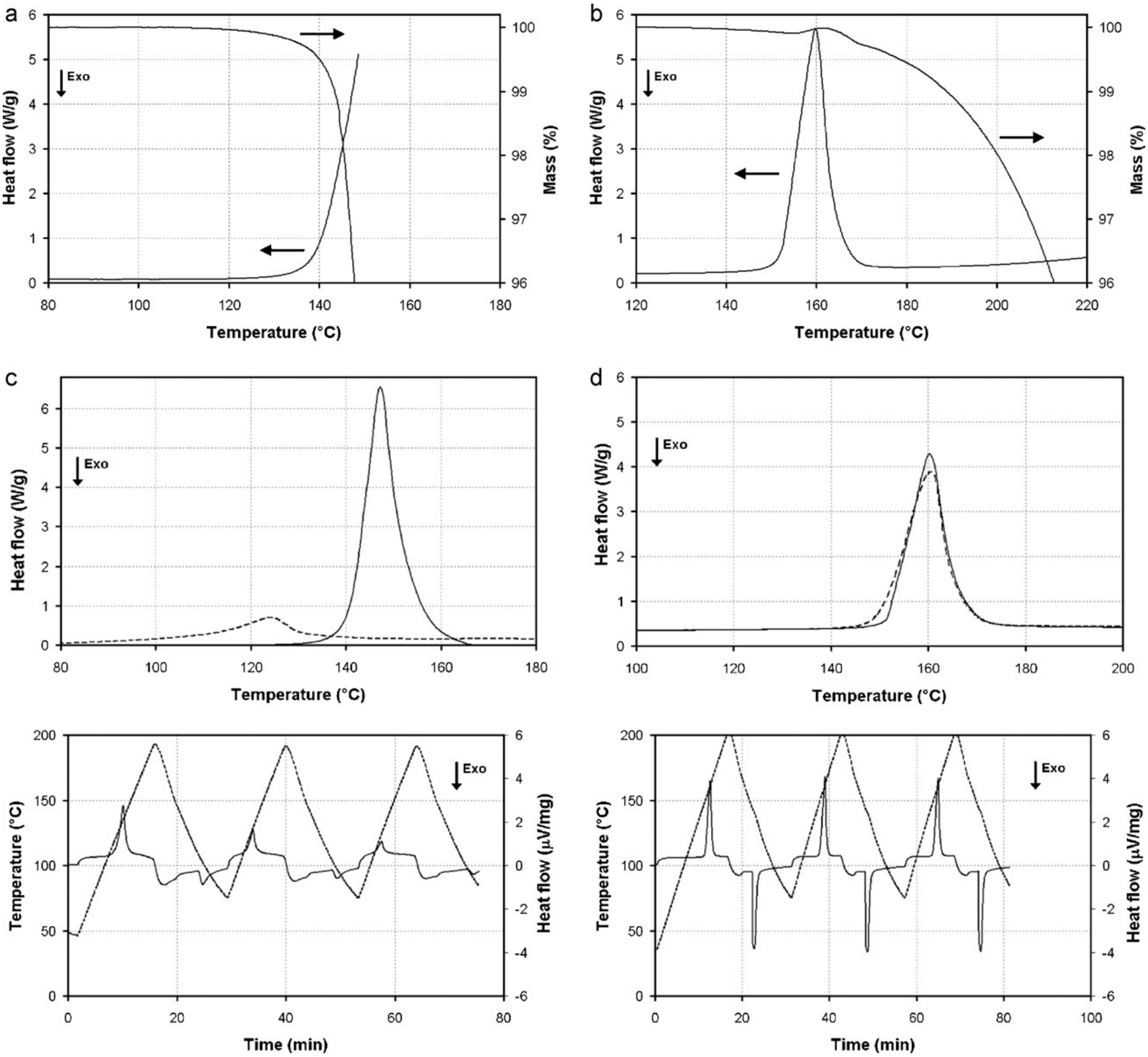

Fig. 3. Maleic and adipic acid thermal analysis measurements. First fusion cycle in open crucible and nitrogen atmosphere: a) maleic acid; b) adipic acid. Initial fifth fusion/solidification cycles in hermetically sealed crucible. c) Maleic acid, d) adipic acid, up, first fusion cycle (straight) and fifth fusion cycle (dotted); down, second, third and fourth cycle (straight), temperature program (dotted).

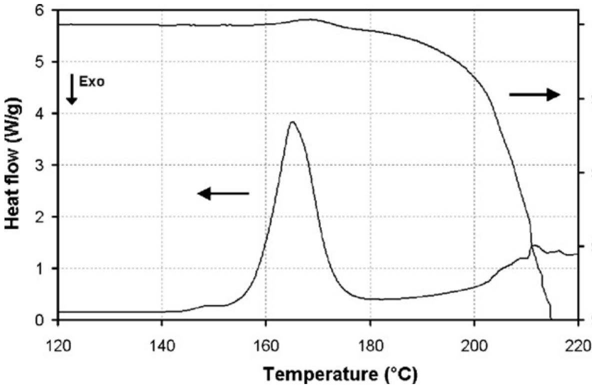

Fig. 4. D-Glucose thermal analysis in open crucible and nitrogen atmosphere.

lar solid–solid transition enthalpy is recorded during the first and the fifth cycle, a mass loss of 5.8% is observed. Furthermore a high subcooling is recorded. In fact, during the cooling phase the solidification peak is registered but, even at 70 °C during the second, third and fourth solidification cycle, no peak corresponding to the solid–solid transition was found (Fig. 1c, bottom).

DMPA presents a relatively low ΔT_{sub} and so no more analysis had been performed in open crucible. However, the material behaviour has been tested in a hermetically sealed crucible (Fig. 1d). Although no mass loss is recorded (due to the hermetically sealed crucible), the PCM exhibit no more solid–solid transition and fusion/solidification peak after the third cycle (Fig. 1d, bottom).

4.2. Dicarboxylic acids

Sebacic acid is the first dicarboxylic acids studied and Fig. 2 presents thermal analysis results in open crucibles in nitrogen (left hand side) and nitrogen/oxygen mixture (right hand side) atmospheres. In both cases, this PCM presents a high enthalpy, 230 J g^{-1}

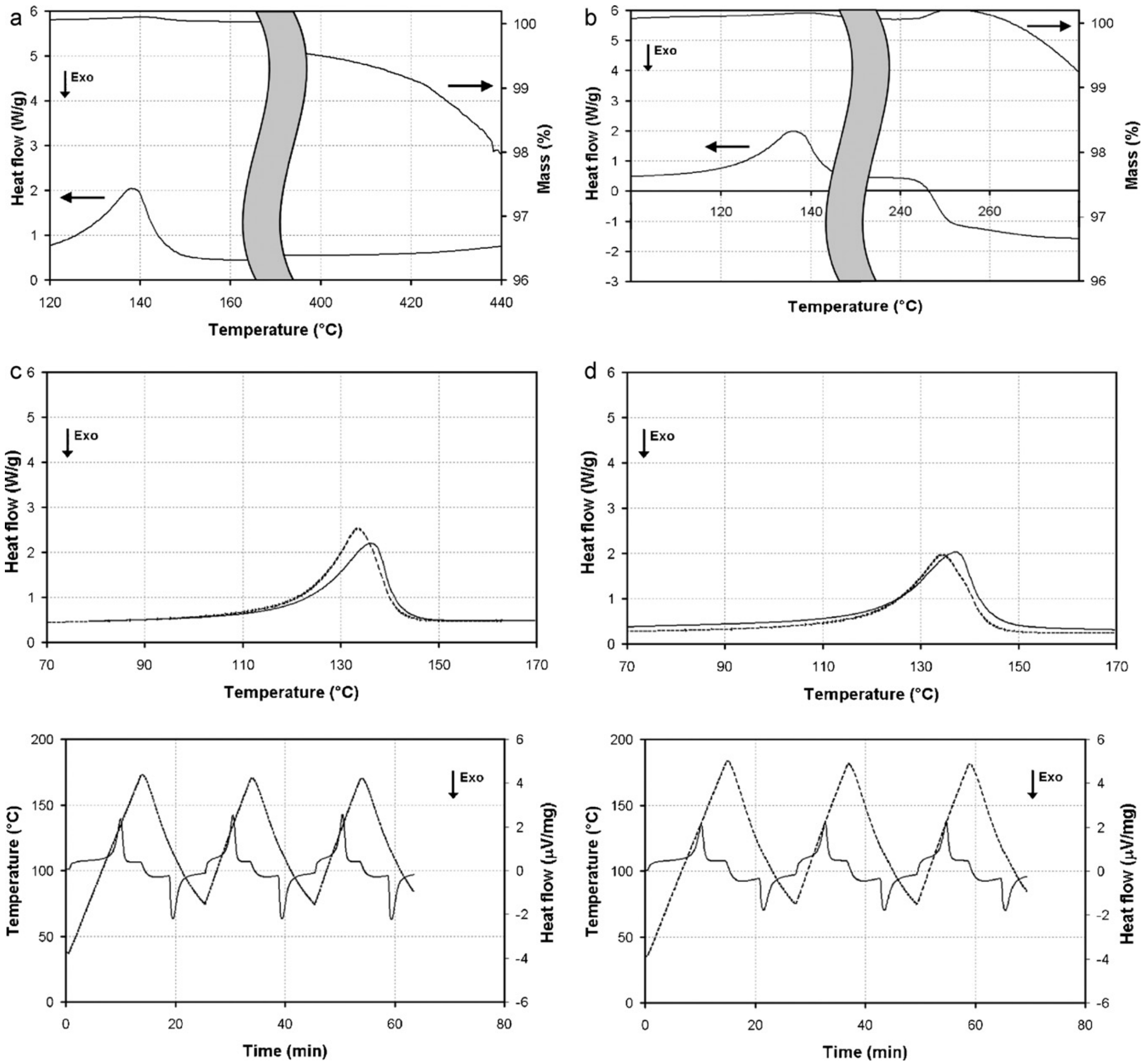

Fig. 5. High density polyethylene thermal analysis in open crucible. First fusion cycle: a) in nitrogen atmosphere; b) in nitrogen/oxygen mixture atmosphere. Initial fifth fusion/solidification cycles: c) under nitrogen atmosphere; d) under nitrogen/oxygen mixture atmosphere. Up: first fusion cycle (straight) and fifth fusion cycle (dotted); down: second, third and fourth cycle (straight), temperature program (dotted).

and a high temperature difference between the onset and the sublimation temperature. The value of ΔT_{sub} is 104 K in nitrogen (Fig. 2a) and 93 K in the nitrogen/oxygen mixture (Fig. 2b). During the cycles performed small mass losses were recorded (not shown). These were 1.6% in nitrogen and 3.5% in oxygen containing atmosphere. These mass losses were confirmed by microbalance measurement. QMS measurements did not reveal a residual gas for this substance at any temperature to explain this mass loss. Sebacic acid showed a subcooling temperature of less than 5 K. It is known that the subcooling phenomena depend on impurity levels. Hence, it can be expected that technical grade materials could have smaller subcooling temperatures compared to the high purity materials utilised in the experiments. In addition, a temperature difference of a few degrees between charging and discharging at this temperature level could be acceptable. Hence, subcooling temperatures of less than 5 K can be considered as small. Fig. 2c on the top shows the first and fifth cycle and on the bottom the second, third and fourth cycle. It can be seen that the cycling stability during the five cycles was generally high.

Fig. 3 presents maleic acid (left hand side) and adipic acid (right hand side) thermograms. Maleic acid begins to melt at 140 °C (Fig. 3c) and adipic acid 12 K higher (Fig. 3d). Both PCMs present a low thermal stability in inert atmosphere (TG-signal in Fig. 3a and b). Hence they have been directly studied in hermetically sealed crucibles (Fig. 3c and d).

Thermograms located in Fig. 3d are related to the adipic acid analysis. The figure on top shows that the peaks, due to the solid–liquid phase change, are similar in the first and in the fifth cycle. The enthalpy value measured is equal to 254 J g^{-1} and the onset temperature remains the same as in the open (non-hermetically sealed) crucible. The subcooling of the sample was less than 5 K.

On the contrary, thermal analysis of maleic acid in hermetically sealed crucible (Fig. 3c) shows a degradation of the latent heat over

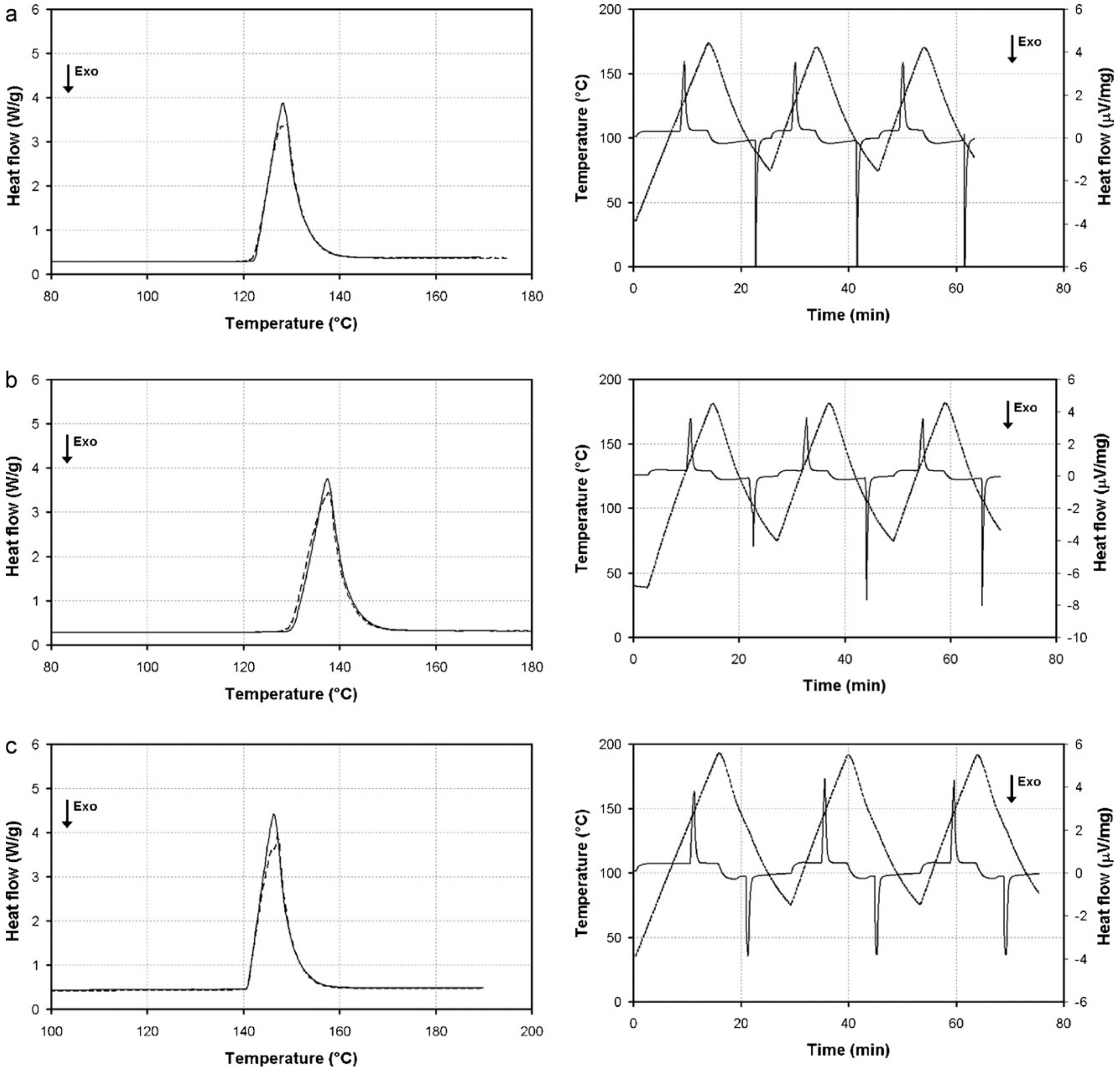

Fig. 6. Aromatic hydrocarbons/arenes thermal analysis in hermetically sealed crucible. a) Benzoic acid; b) phtalic anhydride; c) dimethyl terephtalate. On the left: first fusion cycle (straight) and fifth fusion cycle (dotted); on the right: second, third and fourth cycle (straight), temperature program (dotted).

the fusion/solidification cycle program. In fact, this material has moved from a huge storage capacity (343 J g^{-1}) in the first cycle (straight line in Fig. 3c top) to a much lower record during the fifth cycle of 49 J g^{-1} (dashed line in Fig. 3c top).

4.3. D-Glucose

Fig. 4 shows thermal analysis results of D-glucose in a non hermetically sealed crucible and nitrogen atmosphere. From this figure, the major characteristics of this material can be deducted. The melting temperature is 158 °C and the latent heat is equal to 200 J g^{-1}. The decomposition starts at 190 °C (T_{sub} = 211 °C, ΔT_{sub} = 53 K) and gives rise to a brown coloration of the sample. This decomposition is confirmed by QMS measurements with a strong rise of the signal corresponding to a release of CO_x from about 180 °C.

To conclude the relative low thermal stability of the material does not allow us to consider its use as a PCM. No other thermal analysis has been therefore undertaken on the glucose-D.

4.4. High density polyethylene

Fig. 5a shows TG and DSC results of high density polyethylene (HDPE). In nitrogen atmosphere and open crucible. HDPE presents a very high decomposition temperature of T_{sub} = 448 °C (ΔT_{sub} = 322 K). Thermal cycling performed in the same conditions (Fig. 5c) shows a good fusion-solidification repeatability, with an onset temperature equal to 125 °C, an enthalpy equal to 160 J g^{-1} and a small mass loss (1.7%). As in case of sebacic acid this mass loss cannot be explained from the QMS because no signal was detected.

In the presence of oxygen, Fig. 5b, HDPE presents a much lower decomposition temperature (ΔT_{sub} = 156 K). The enthalpy and the melting/solidification temperature of the cycle remained the same in the presence of oxygen compared to inert conditions (Fig. 5d).

Thermal analysis performed on HDPE confirmed observations from the literature review (Section 2): HDPE is potentially a good storage material. However further investigation must be performed

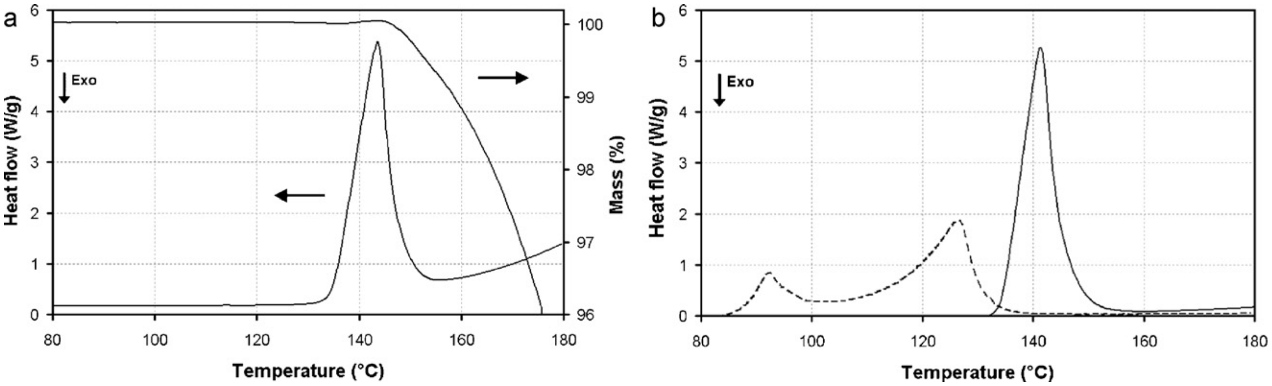

Fig. 7. Urea thermal analysis. a) In open crucible and nitrogen atmosphere; b) in hermetically sealed crucible: on left: first fusion cycle (straight) and fifth fusion cycle (dotted); on right: second, third and fourth cycle (straight), temperature program (dotted).

in order to explain the recorded mass losses and the long term stability.

4.5. *Aromatic hydrocarbons/arenes*

Aromatic hydrocarbons have been first studied in nitrogen atmosphere. Results are not presented here but showed a low sublimation temperature, with a ΔT_{sub} of approximately 12 K and therefore measurements in non hermetically sealed crucible are prohibited. A thermal analysis of aromatic hydrocarbons using closed crucible was performed and Fig. 6 presents the obtained thermogram for benzoic acid (Fig. 6a) phthalic anhydride (Fig. 6b) and dimethyl terephtalate (Fig. 6c). Fig. 6 on the left shows the first fusion cycle (straight line) and the fifth fusion cycle (dotted line). Fig. 6 on the right shows the second, the third and fourth full cycle vs. time with its temperature program. Although the melting temperature of these PCMs is somewhat different (benzoic acid, Fig. 6a, $T_{\text{on}} = 123\,^\circ\text{C}$; phthalic anhydride Fig. 6b, $T_{\text{on}} = 130\,^\circ\text{C}$ and dimethyl terephthalate Fig. 6c, $T_{\text{on}} = 141\,^\circ\text{C}$), solid–liquid transitions of the three acids studied showed similarities. All of these materials present a latent heat approximately equal to about $150\,\text{J}\,\text{g}^{-1}$. The enthalpy of each respective material remains stable after 5 cycles. Indeed the values measured at the fifth cycle differ not more than 5% from the initial results. Although no loss of mass is measured for the benzoic acid and phthalic anhydride, in the case of the dimethyl terephthalate the crucible has not remained hermetic. Hence, a 2% mass loss has been recorded between the second and the fourth cycle. It may be due to the higher value of the maximum temperature reached by the sample (190 °C) during this measurement.

4.6. *Other: urea*

Thermal analysis of urea, in non hermetically sealed crucible and in nitrogen (Fig. 7a) presents a material with a high storage capacity ($220\,\text{J}\,\text{g}^{-1}$) and a melting temperature at $T_{\text{on}} = 135\,^\circ\text{C}$. The decomposition temperature is relatively low ($\Delta T_{\text{sub}} = 37\,\text{K}$). As in the case of aromatic hydrocarbons previously presented, the study of urea had been pursued by analysis in a hermetically sealed crucible (Fig. 7b). After five fusion/solidification cycles no mass losses are observed. However the latent heat and also the shape of the peak differed. Initially the fusion peak is narrow, located at 134 °C and with a related enthalpy equals to $216\,\text{J}\,\text{g}^{-1}$. After five cycles, the peak has a different shape. It is in fact composed of two large peaks, one around 90 °C with an enthalpy equal to $25\,\text{J}\,\text{g}^{-1}$ and the other one around 125 °C with $102\,\text{J}\,\text{g}^{-1}$. It can be concluded, as previously published by Kamimoto et al. [43], that urea is then subjected to degradation with temperature, even in hermetically sealed crucible.

5. Conclusion and summary

A general literature review has allowed us to identify organic PCMs in the temperature range from 120 to 150 °C. Two of these candidates are solid–solid transition materials (SSTMs), tris(hydroxymethyl)aminomethane (TAM) and dimethylpropionic acid (DMPA), and nine are phase change materials (PCMs) with solid–liquid phase change. Among them three dicarboxylic acids (sebacic, adipic and maleic acid), a sugar (D-glucose), a polymeric hydrocarbons (HDPE), three aromatic hydrocarbons (benzoic acid, phthalic anhydride, dimethyl terephthalate), and finally urea have been selected. To determine the main characteristics of these storage materials a simultaneous thermogravimetry (TG) and differential scanning calorimetry study, commonly called STA, has been conducted. In addition coupled gas analysis with a quadrupole mass spectrometer (QMS) was utilised. The analysis was carried out in aluminium crucibles (hermetically sealed or open) under different atmospheres (inert and in the presence of oxygen).

Conclusion of this study is that from the eleven selected materials, the following four show unsuitable characteristics for latent heat storage materials:

- DMPA, maleic acid and urea did not show a suitable cycling stability over five cycles in hermetically sealed crucible;
- As previously published, thermoanalytical investigation of D-glucose indicated a low decomposition temperature even in nitrogen atmosphere.

The remaining seven materials are judged as follows:

- TAM presents suitable properties, but also high transition subcooling and further studies must be performed in order to assess and overcome this tendency using technical grade material or nucleating agents;
- Sebacic acid and HDPE are thermally stable in nitrogen and air over five cycles, 50 K above the transition temperature. However a small mass loss was detected, which cannot be explained by the QMS. Further long term cycling tests are needed to prove long term stability;
- Adipic acid, benzoic acid, phthalic anhydride and dimethyl terephthalate can only be used in hermetically sealed crucibles. Under these conditions they showed a stable and reversible phase change. Strategies for realizing technical solutions in inert atmosphere and closed systems need to be investigated.

The paper emphasized the importance of measurement conditions to qualify PCMs (open/closed crucible, type of atmosphere). The work contributes to a practical methodology to identify suitable high-temperature PCMs susceptible to decomposition. From the results it can be derived that, from the identify PCM, only few organic materials show a potential to be applied in the temperature range 120–150 °C. Further investigations concerning long term stability are required.

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