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Grau de Química

Treball Final de Grau

Degradation study of bio-based phase change materials to improve the energy efficiency of active systems.

Estudi de la degradació de materials de canvi de fase d'origen vegetal per a la millora de la eficiència energètica en sistemes actius.

Ricard Sánchez Valls

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M’agradaria donar les gràcies a les meves tutores d’aquest treball de fi de grau, Camila i Inés per acompanyar-me aquest últim semestre, i als integrants del grup DIOPMA per ajudar-me en tot el que necessitava.

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REPORT

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1. SUMMARY

Nowadays, sustainability is one of the most important fields of research due to the importance of making a profitable use of the planet resources. In many fields are working to develop new ways to improve energy efficiency. This is the case of development in phase change materials, a type of chemical substances which contribute to a better efficiency of the thermal energy storage in systems like buildings or refrigerate compartments.

There are different materials that can be used as phase change materials, but bio-based materials are very interesting to overcome those made by fossil fuel, for their sustainable characteristics. However, bio-based PCM commercially distributed have been not investigated in deep and due to the lack of investigation on them, these phase change materials implementation in actual buildings is low. One of the principle problems of these materials is the lack of information about their degradation towards daily thermal conditions in a real building.

This work focuses in the study of degradation of two fatty acids used as PCM, capric acid and myristic acid, in order to evaluate if their structure or their thermo-physical properties change after two different types of thermal treatments which try to reproduce the daily conditions of a building.

Some similar investigations have been previously done on fatty acids degradation, but they focused characterization on infrared spectroscopy, not being able to determinate a structural change on the fatty acids molecules. In this work, further characterization is done, such as DSC and TGA to analyse thermo-physical properties, rheometry to determinate changes in viscosity, and gas chromatography with mass spectrometer detector to obtain better results in structural characterization.

Keywords: thermal energy storage, phase change materials, fatty acids, degradation, materials characterization, DSC, TGA; FT-IR, Chromatography, Rheometry.

2. RESUM

Avui dia la sostenibilitat és un dels camps més importants en la investigació per la importància de fer un millor ús dels recursos del planeta. En molts camps treballen per desenvolupar noves maneres de millorar l'eficiència energètica, com en el cas dels materials de canvi de fase, substàncies químiques que contribueixen a la millora d'eficiència en sistemes d'emmagatzematge d'energia tèrmica com edificis o cambres frigorífiques.

Hi ha diferents materials que es poden fer servir amb aquest propòsit, però els d'origen vegetal són molt interessants per imposar-se als d'origen fòssil per les seves característiques envers la sostenibilitat. Aquest tipus de materials de canvi de fase d'origen vegetal no s'apliquen encara en edificis per la falta de recerca. Un dels principals problemes és la falta d'informació sobre la seva degradació en casos d'edificis reals.

Aquest treball es centra en el estudi de la degradació de dos àcids grassos que es fan servir com a materials de canvi de fase, el àcid capric i l'àcid mirístic, per avaluar si la seva estructura o propietats termofísiques varien en aplicar dos tipus de tractaments tèrmics que busquen reproduir les condicions diàries que patirien en un edifici convencional.

Hi ha investigacions prèvies sobre la degradació de àcids grassos semblants, però la caracterització es centren en espectroscòpia infraroja, la qual no permet veure cap canvi estructural. En aquest treball fem un pas endavant, fent servir DSC i TGA per analitzar les propietats termofísiques, reometria per determinar canvis en viscositat, i cromatografia de gasos amb espectròmetre de masses com a detector per obtenir millors resultats en la caracterització estructural.

Paraules clau: Emmagatzematge d'energia tèrmica, materials de canvi de fase, àcids grassos, degradació, caracterització de materials, DSC, TGA, FT-IR, cromatografia, reometria.

3. INTRODUCTION

In matters of technologies designed to improve energy efficiency, thermal energy storage (TES) and effective heat utilization are very important in order to obtain a correct use of the energy destined to provide heat, with a reduction in the consumption of energy used and without compromising the utility of the system. Most of these TES systems are applied in places where it is interesting to keep a constant temperature or with low fluctuations, such as buildings or refrigerating chambers, even if the purpose is to cool or heat [1,2,3,4].

TES can be implemented in buildings by sensible heat storage (SHTES) and by latent heat storage (LHTES). The first one refers to the systems where there is an exchange of heat with an associated change of temperature of the material implemented, whereas, in the second one there is not a temperature change of the material because there is a phase change (Figure 1). In terms of efficiency, the latent heat storage is far more efficient that the sensible heat storage because it has higher storage density, which means that can store the same amount of energy in less volume [1,2]. Moreover, as consequence of the constant temperature during the phase change, these materials have very potential in applications such as stabilization of temperatures in closed spaces.

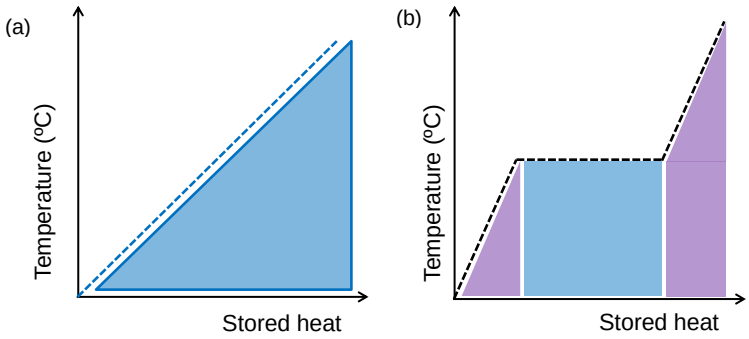


Figure 1.Thermal energy storage profile vs. Temperature when heat is stored as sensible heat (a) or latent heat (b). (Image extracted from Barreneche, C. ref 5)

Latent heat storage can be incorporated in form of phase change materials (PCM), in a passive way which demands to be encapsulated for their technical use, or in an active system like being pump in a circuit [1].

There is also a third group of TES which consist in thermo-chemical energy storage (TCTES). However, this type of materials are less used because their difficulty to work with, and their high number of thermal requirements [5].

3.1. PHASE CHANGE MATERIALS

PCM are some chemical substances which are able to absorb or release latent heat thermal energy while temperature maintains constant during the physic state change, even if it is solid-liquid or liquid-gas, which make them a nearly isothermal storage of heat. When temperature increases, PCM melt in an endothermic reaction, absorbing heat, and keeping the temperature nearly constant. Otherwise, when temperature decreases, PCM release heat in an exothermic reaction and returns to the solid state.

Moreover, PCM have large TES density, a property which make them very interesting to be implemented in systems referred before such as buildings to help maintaining the inside temperature, having as result a better energetic efficiency with the reduce of an active system, like the heating system, with the use of a passive system like the implementation of these substances [2,3,4].

So basically, PCM are substances able to store and release heat in order to delay the peak temperature indoors in buildings, to reduce the peak indoor temperature, and to achieve energy savings. These are the main claims to install PCM in building facades.

In terms of substances that fit properly as PCM for latent heat storage, some properties are required in more or less extent [1]. Those are:

- High latent heat of fusion per unit of volume and weight, in order to reach a high TES density and improve the efficiency.

$$Q_{latent} = \int_{T_1}^{T_{pc}} C_{p,s} \cdot dT + \Delta H_{pc} + \int_{T_{pc}}^{T_2} C_{p,l} \cdot dT$$

This is the equation corresponding to the latent heat. As it is expressed, this heat depends on the enthalpy of the phase change and specific heat capacity of both phases.

- A melting point that suits with the temperature needed in their application.

- Low vapour pressure at work temperature to prevent problems in the encapsulation.

- Non-toxic, nor inflammable, corrosive or dangerous. It is required a chemical stability.

- A low subcooling degree for the phase change at the estimated temperature.

- Low rate of degradation with time or after cycles of solidification and melting.

- High thermal conductivity to guarantee the desired absorption and emission of energy of the storage system.

- A reproducible crystallisation to obtain a cyclic stabilisation.

There are not materials that satisfy all of these properties, but there are some which approach a lot. I am going to focus on those which its phase change is from solid to liquid and vice versa, which are the most used because of their high phase change enthalpies, and their high capacity to be controlled in terms of volume change and durability. In this group PCM are differentiated between organic and inorganic substances [1,2] (Figure 2).There are also metals that can be considered as a third group, but are commonly referred as inorganic substances[2,3].

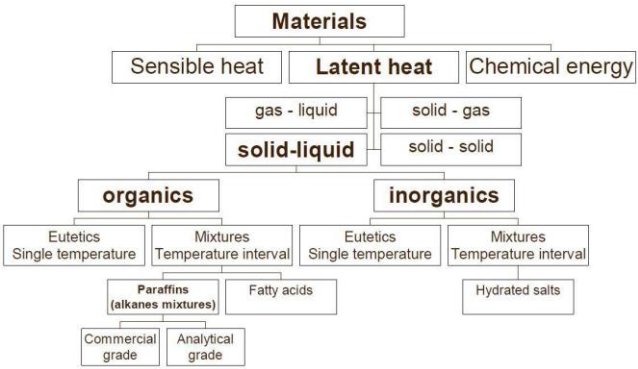


Figure 2.Classification of TES materials. (Image extracted from Cabeza, L.F. et. al, ref 1)

The inorganic materials have better energy density and thermal conductivity. However, they show problems of corrosion, subcooling and phase separation which translates into lack of thermal stability. An example of inorganic substance could be the hydrated salts [1].

Even if organic substances present lower values of TES density and conductivity, and they are highly volatile and flammable, some additives can be added to improve their characteristics, and their great advantages are their chemical and thermal stabilities. Nowadays, the most commercialized organic substances used as PCM are paraffin waxes, which are a mixture of pure alkanes that present good results at a low price. However, there are other organics substances that present the mentioned properties, and that are not used as much as paraffin, fatty acids [1].

The solid-liquid phase change materials require to be encapsulated due to their tendency to leak, and because they change their physical properties from one state to another [3,6]. There are two types of encapsulation, micro and macro. The most commonly used is the macro encapsulation which consist in encapsulate the PCM in a container that can have different shape such as a tube or a sphere [1,3].

The selection of the material depends on the application for what it is used to, because every substance has its own melting point on a range of temperatures. In buildings, for example, hydrated salts are not commonly used because they are corrosive, and they can affect the whole structure. However, in this case, paraffin and fatty acids are more suitable because of their chemical and thermal stability, added to their low vapour pressure, non-toxic and non-corrosive character, and high latent heat capacity [1,4].

This project is focused on bio-based PCM. These PCM have not fossil fuel origin and their environmental impact is lower. Therefore, the selected PCM were fatty acids. The structure of a fatty acid consists in a carboxylic group joined to a non-polar hydro carbonated tail. This tail can be saturated if only contains simple bonds, or unsaturated if it has one or more double bonds. Fatty acids differ from each other depending on the length of their hydro carbonated tail, and the presence, the number and the position of double bonds. The carboxylic group always stays on the first carbon [7].

The properties of fatty acids depend on the length of the tail and the number of double bonds. Longer chain of carbon results into higher melting points, and unsaturated fatty acids have lower melting point than saturated. That is because de double bonds in natural fatty acids are *cis* and this result into a turn in the hydro carbonated tail, making them less flexible and more difficult to pack [7].

In TES building systems, long term stability (LTS) of the PCM plays a key role because it is what determines if it is reliable or not. PCM are placed inside the outer walls of the building, a high degradation of the material suppose a descent on the energy efficiency, and the consequent substitution, which result into a big investment [1,2].

Degradation is referred to a change on the structure of the molecule and the respective changes in their properties. This change can be produced by consecutive cycles of heating and cooling, liquidation and solidification. After lots of those cycles the molecules can polymerize, ramify, and so on.

Although degradation is a threatening problem for PCM systems, there is not many information about. One principle reason is that PCM are innovative materials, which are not usually applied, and because of it, there are few real cases.

In addition, researchers have commonly used FT-IR to analyse the decomposition of fatty acids under thermal treatments. However, they do not see any changes in the chemical structure, since the degraded compounds have the same functional groups than the original fatty acids.

In this project, for the first time, we purpose a new methodology to follow the degradation of fatty acids by applying rheometry and gas chromatography as complementary characterisation techniques, to demonstrate that fatty acids degrade after thermal treatments.

4. OBJECTIVES

The general aim of this project is to determinate if two fatty acids used as PCM in buildings, myristic acid and capric acid; degrade after two types of thermal treatments. These consist in a long exposure of the fatty acids at higher temperatures than the melting point, and on the other hand, heating/cooling thermal cycles in order to simulate oscillation daily conditions of a building.

To achieve this principle objective, characterization of the initial and final samples must be carried out before and after thermal treatments. The characterization includes rheological analyses, FT-IR and chromatography composition analyses, differential scanning calorimetry and TGA.

5. EXPERIMENTAL SECTION

5.1. MATERIALS AND METHODS

In this project, two different free fatty acids used as PCM in buildings were selected to be studied:

Entry	Fatty acid	CAS number	Molecular formula	Supplier	Molecular weight [g·mol^{-1}]	Melting range [ºC]
1	Capric acid	334-48-5	$C_{10}H_{20}O_2$	Sigma - Aldrich	172,26	27 - 32
2	Myristic acid	544-63-8	$C_{14}H_{28}O_2$	Merck	228,37	52 – 56

Table 1.Fatty acids information.

In order to analyse how these two compounds degrade, two different experiments were carried out, involving the degradation towards constant temperature at long exposition to evaluate thermal stability, and degradation towards cycles of heating and cooling to evaluate cycling stability.

5.1.1 Thermal stability

Four test tubes, two for each fatty acid, were filled and introduced into a laboratory water bath at a constant temperature of 60ºC. All tubes were sealed with parafilm to avoid losses. This experiment consists in maintaining the material at a constant temperature during 100 hours and 500 hours, to determinate the thermal stability of the materials, comparing the initial and the final properties, and characterizing the product to observe if there is any difference with the initial compound.

The sample corresponding to the 500 hours treatment of myristic acid was not completely sealed, and the final product had some humidity due to the water of the thermostatic bath.

5.1.2 Cycling stability

This test was performed to study changes in phase change materials after a large exposure to thermal cycles of heating and cooling in order to reproduce the daily conditions of a material applied in a building.

PCM were cycled in a thermocycler Bioer Gene Q T-18. The samples were contained in eight eppendorf of 0,6mL, sixteen in total counting both fatty acids. Each cycle consist in heating the sample during 10 minutes at 70ºC, and then cooling them to 15ºC and spend 10 minutes more, with a ramp of temperature of 0,5 ºC/min (Figure 3). Half of the samples were retired after 500 cycles, and the other half performed 1000 cycles.

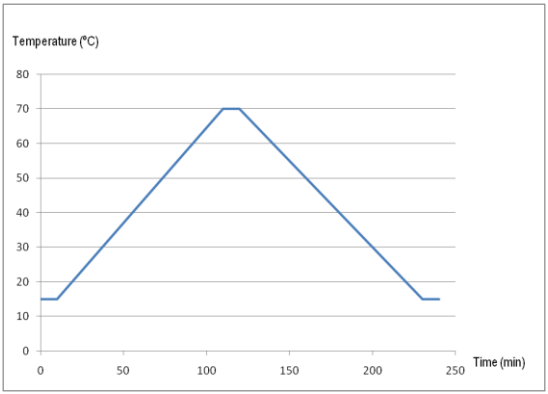


Figure 3.Cycle of Temperature vs. Time of the cycling stability treatment.

5.2 CHARACTERIZATION TECHNIQUES

5.2.1 Structural characterization

FT-IR

Infrared spectroscopy is a technique usually used in qualitative analysis to determinate functional groups of a sample and it structure, although it can also be used in quantitative analysis, but not in this project.

This technique gives structural information from the interaction between the material and IR radiation, measuring the vibration frequencies of the bonds of the atoms in a molecule. To observe a molecule in the IR, it must be a variation in de dipole moment, a polar molecule is required. Moreover, the energy gap must correspond to the energy of the radiant beam.

The Fourier Transform Infrared equipment presents some advantages from the classic IR. Monochromator is no longer needed, so all wavelengths arrive simultaneously to the detector, reducing the number of optical components, and improving the signal/noise relation, which results in a higher resolution and a very accurate signal.

The analysis of the functional groups has been made by Fourier transformed infrared spectroscopy using a Spectrum Two™ from Perkin Elmer, coupled with attenuated total reflectance (ATR). The equipment standard spectral resolution is 0,5 cm^{-1} and the characterization was done in a wavelength range of 4000 – 450 cm^{-1}.

Gas Chromatography

This analytical technique is used to separate volatile compounds and characterize them with the complementation of some sort of detector, depending on the application and the substances analysed.

The gas chromatography consists in a gas mobile phase (He, Ar or N_2), which is pumped at certain conditions of pressure and temperature. The sample is also injected to the equipment with an injector in liquid phase, but it is instantly evaporated by the implementation of heat. Then the sample is transported through the equipment by the mobile phase, which does not interact with the analyte. The separation of the different compounds of the sample is executed in the column. Columns contain the stationary phase which is the responsible of the separation. There are different types of columns depending on the interaction with the solute, but the most important ones are those that the stationary phase is chemically linked with the column. The separation is due to polar character of the stationary phase, and the compounds of a sample are separated by their polarity.

In this project it is used a gas chromatograph – mass spectrometer Shimadzu QP2010, using He as mobile phase at 1ml/min flow, and a stationary phase BP-21. The chromatography has been realized by *Unitat de Cromatografía dels Centres Científics Tècnics de la Universitat de Barcelona.*

5.2.2 Rheological measurements

Rheology studies the flow and deformation of a material under external forces with the purpose to obtain information about the rheological properties of the substance such as viscosity or viscoelasticity. This measurement is realized with a rheometer, and the analysis can

be done in different conditions of temperature, time, stress and strain, which affect directly to viscosity.

A shear rheometer was used to determine viscosity. The equipment used was a RST cone plate rheometer from AMETEK Brookfield, added to a Peltier air as control temperature device. This rheometer has a maximum torque of 100 mN·m, and a resolution of 0,15 μN·m.

Measurements were done at constant temperature, in a constant ascendant ramp of shear rate:

Entry	Fatty acid	Shear rate [s^{-1}]	Time [s]	Measurement points	Temperature [ºC]
1	Capric acid	1000 - 5000	300	100	35
2	Myristic acid	1000 – 5000	600	150	60

Table 2. Rheometer experimental conditions

5.2.3 Thermal properties characterization

Differential Scanning Calorimetry

DSC is used to study the thermo-physical properties of a substance, such as latent heat, melting and solidification temperature, phase change enthalpies, or specific heat capacity.

The equipment has two melting crucibles, one empty and used as the reference, and the other with the substance to analyse (sample). Then it is programmed an ascendant ramp of temperature versus time, and we observe the difference between the two melting pots to obtain a signal.

Thermo-physical properties, such as melting temperature and enthalpy of fusion, were determined by differential scanning calorimetry, using a Mettler Toledo DSC822e instrument under N_2 flow. All samples were firstly introduced into 40μL aluminium crucibles, with the determination of the weight using an analytical balance. The analyses were performed between 10-70 ºC, under 0.5 ºC/min heating rate and 50 ml/min N_2 flow (see Figure 4).

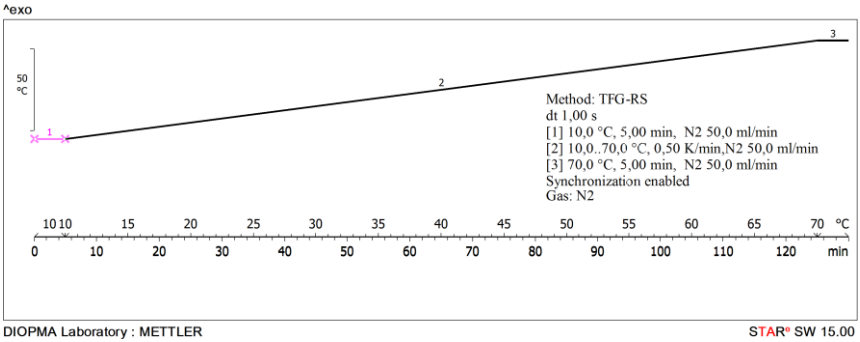


Figure 4. DSC program used for characterisation of both fatty acids.

Thermo-gravimetric analysis

This technique is usually used to determinate degradation of compounds by measuring the percentage of total weight loss of a sample under a temperature increment in a controlled atmosphere. TGA instruments consist in a furnace where inside there is a pan supported by a precision balance. Samples are placed on the pan and then the heating process initiate. During the process the balance records the weight of the sample, while temperature increases.

In this project, TGA analysis is used to determinate the upper use temperature of both fatty acids, and the products from the thermal treatments, and compare them. This temperature mentioned refers to the point where an increase in temperature results into a degradation of the material, and also it is the point where 1,5% in weight of the sample is lost. The instrument used in this characterisation is a TGA/DSC DSTQ600 from TGA Instruments. The analysis was performed between 50-300ºC, with a 10ºC/min heating ramp, under a constant flow of synthetic air of 50mL/min, and were used around 10mg of sample contained in 100µL alumina crucibles.

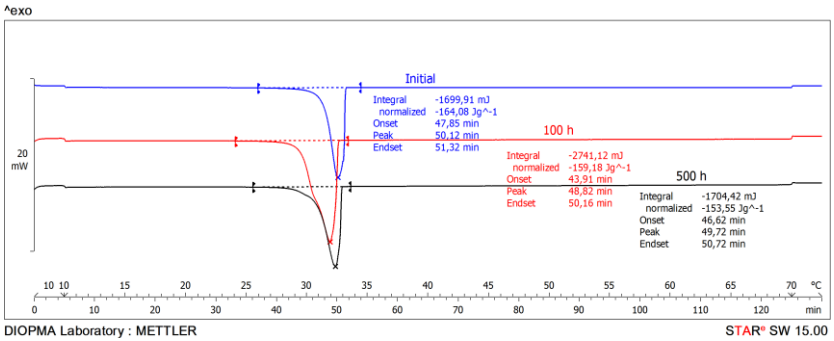
6. RESULTS AND DISCUSSION

6.1 Thermo-physical properties

DSC

Melting enthalpy and melting temperature were measured for both fatty acids, and the products from the thermal stability and the cycling stability treatments. Figure 5 shows the results obtained, comparing the initial fatty acid and the different products of a same treatment, in order to evaluate the evolution along the experiment, and see the changes in this thermo-physical properties.

a)



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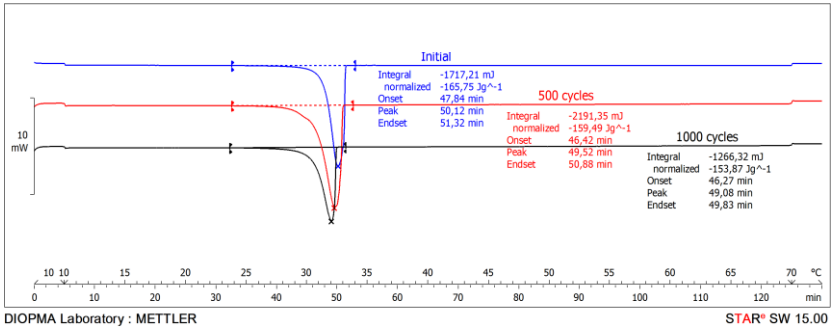


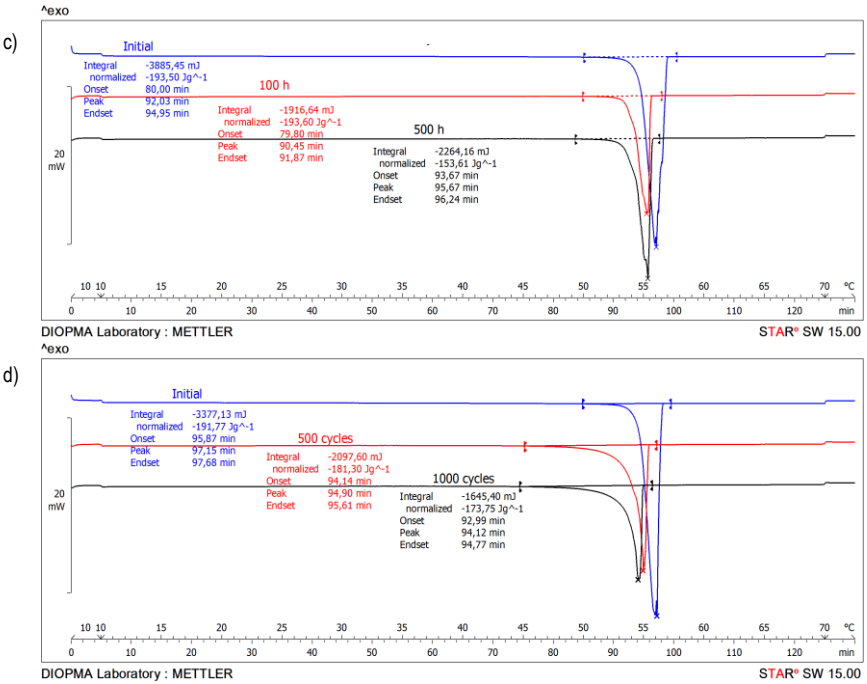


Figure 5. DSC results: a) Capric acid thermal stability, b) Capric acid cycling stability, c) Myristic acid thermal stability, d) Myristic acid cycling stability

As DSC analysis shows, there is a general trend in both fatty acids to reduce the melting point after the two treatments. This reduction supposes a change of nearly 5% respect the initial phase change temperature in the case of the capric acid after 500 hours, which is the most accentuated case. Even if in most samples there is only one Celsius degree of difference or less, being the melting point such an important property for a PCM because of their application, we can consider this reduction as a representative decrease in the thermo-physical properties. This change could be explained as such degradation of the fatty acid chemical chain during the thermal treatment that distorts the measured temperature, in this case.

Moreover, it can be observed the same tendency in melting enthalpy. There is also a reduction in this property after the treatments, which directly affects to the latent heat of the PCM. A decrease in melting enthalpy supposes a decrease in latent heat, with the result of a PCM with less capacity to accumulate heat, and reducing the efficiency of the whole TES system. Therefore, the compound degradation is affecting the main thermo-physical properties

and this must be known before their implementation. In addition, deep studies need to be performed by considering more thermal cycles or hours under such a temperature since the samples do not reach a stagnation state with the thermal treatment performed in this project. Further research is suggested.

Despite observing a decrease of melting enthalpy in myristic acid after 500 hours of thermal stability treatment, due to the sample was wet, we cannot affirm that this reduction is because to a change in the thermo-physical properties of the fatty acid.

Sample	Nº hours	ΔH_m [J·g^{-1}]	ΔH_m [%]	T_m [ºC]	T_m [%]
Capric acid	0	164		32,3	
	100	159	-3	31,5	-2,3
	500	154	-6	30,7	-5,0
Myristic acid	0	194		55,3	
	100	194	0	54,8	-0,9
	500	-	-	-	-

(a) 500 hours myristic acid sample was wet, and results are not representative.

Table 3. DSC thermal stability results.

Sample	Nº cycles	ΔH_m [J·g^{-1}]	ΔH_m [%]	T_m [ºC]	T_m [%]
Capric acid	0	166		32,3	
	500	159	-4	32,0	-0,3
	1000	154	-7	31,8	-1,4
Myristic acid	0	192		55,3	
	500	181	-5	54,6	-1,3
	1000	174	-9	54,2	-1,9

Table 4. DSC cycling stability results.

Therefore, based on the obtained results, the thermal stability is ensured in myristic acid while affects the phase change enthalpy of capric acid up to 6%. Furthermore, the cycling

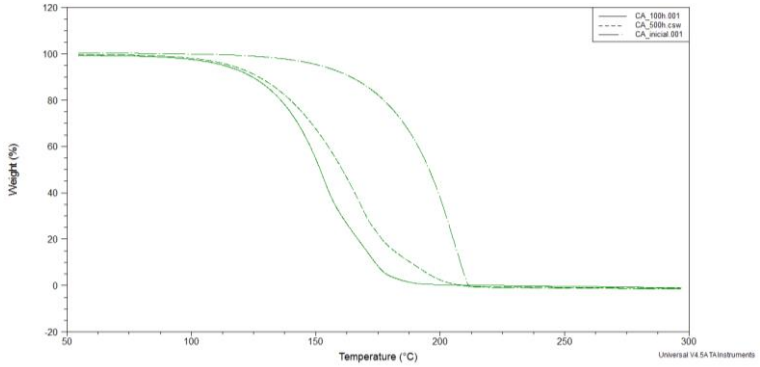
stability test affects both fatty acids under study by decreasing their enthalpy around 7% for capric acid and 9% in the case of myristic acid.

TGA

As it is previously mentioned, this analytical technique is used in this project to determinate the upper use temperature of both fatty acids before and after the thermal treatments. Although it does not give structural information, a change in this property can be related to some sort of change in the fatty acid molecule, and so to a degradation because of the thermal treatment.

The results for the TGA are shown in Figure 6 and Table 5:

a)



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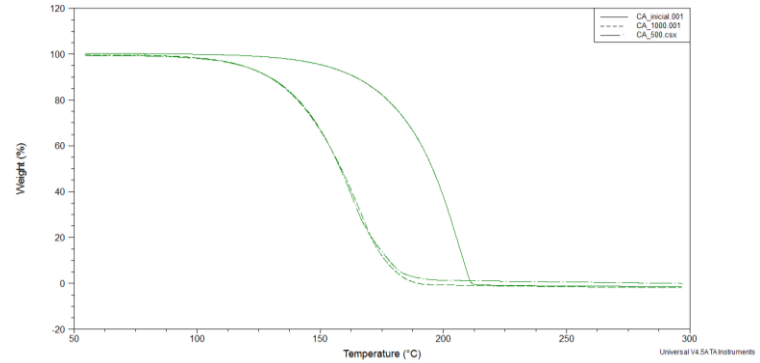


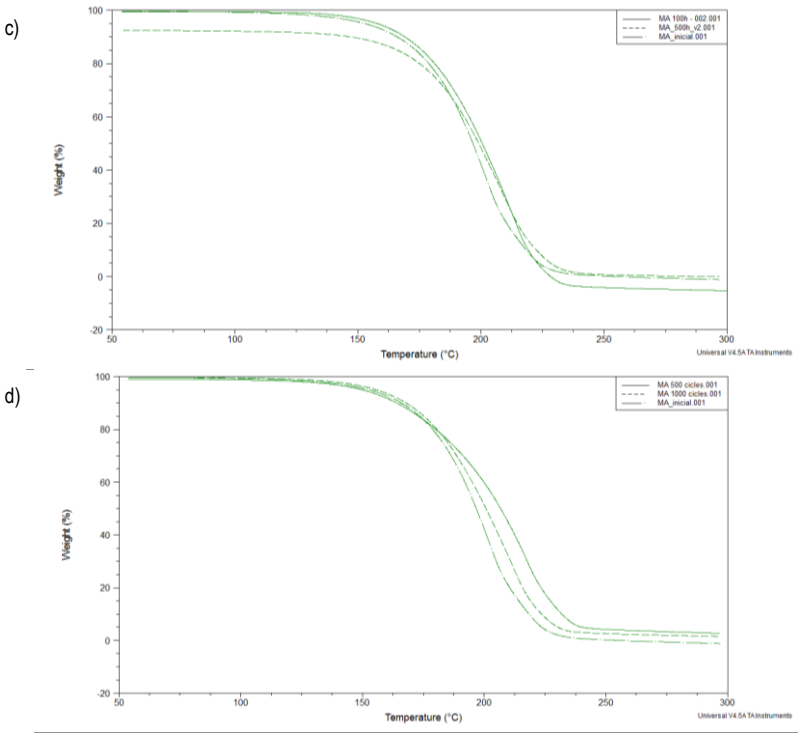


Figure 6. TGA results: a) Capric acid thermal stability, b) Capric acid cycling stability, c) Myristic acid thermal stability, d) Myristic acid cycling stability

Sample	Nº hours	Upper working Temperature [ºC]	Nº cycles	Upper working Temperature [ºC]
Capric acid	0	128,3	0	128,3
	100	98,2	500	102,2
	500	99,2	1000	101,9
Myristic acid	0	129,4	0	129,4
	100	131,8	500	142,4
	500	136,4	1000	136,4

Table 5. TGA numerical results

As the graphics and the numerical results show, there is a significant difference between the initial fatty acids and their corresponding thermal treated samples. The difference is remarkable in the capric acid, with a descent of near 30ºC in the upper working temperature. There is also a change in myristic acid, although it is less pronounced, and the behaviour is different than the capric acid because there is a rise in the upper use temperature instead of a descent. Thereby, the maximum working temperature for capric acid is around 100 ºC and for myristic acid is around 135 ºC. This fact, joined with the changes observed in the DSC analysis, leads to think of a degradation of both fatty acids molecules.

Notice that, the thermal treated samples degradation process changes to steepest slope in the case of capric acid, highlighting that the thermal treatments accelerate the thermal degradation. Moreover, this is in concordance with other results obtained by DSC. This behaviour is stabilized and there are almost non-difference between 100 and 500 hours treatments and 500 and 1000 thermal cycles.

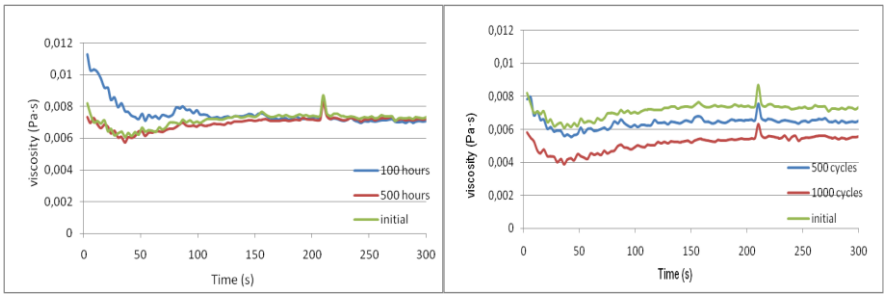
6.2 Rheological analysis

This part of the characterization allows determining how the liquid phase behaves, and a change in viscosity involves a change in the molecule.

The results show a Newtonian behaviour in all samples, with a slight decrease of viscosity at the beginning of the analysis. However, as these fatty acids have low viscosities [mPa·s] this initial behaviour is negligible.

As it can be seen in Figure 7, only the sample of capric acid exposed to a cycling stability treatment changes the viscosity over cycles. The decrease of this property while the increase of thermal cycles is a signal of degradation of the capric acid molecule and this is in concordance with the results obtained by DSC and TGA. On the other hand, it is not appreciated any viscosity change on the samples of myristic acid, or in the thermal stability sample of capric acid.

a)



b)

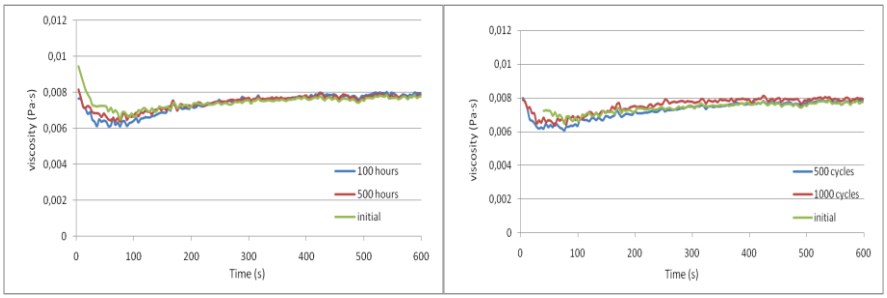


Figure 7. Rheometer results: a) capric acid b) myristic acid

6.3 Structural analysis

FT-IR

In a previous analysis of both fatty acids molecule structure, some peaks should be easily predictable to determinate. Before 3000 cm^{-1}there should be a peak corresponding to sp^3 C-H stretching, and at near 1715 cm^{-1} the peak of a C=O stretching vibration signal. Moreover, because of the carboxylic acid group, there should be a long range signal between 3500 cm^{-1} and 2500 cm^{-1} approximately. Lower wavelength peaks should be seen at approximately 938 cm^{-1} corresponding to the out of plane bending vibration, and at 721 cm^{-1} corresponding to the inplane swinging vibration of –OH functional group [8].

In addition, capric acid and myristic acid share the same functional groups, and they only differ in the length of the molecule, so the IR spectre should be the same.

As expected, infrared spectroscopy do not appreciate any change in the structure of the fatty acids (Figure 8). Products after thermal treatments share the same exact peaks that the initial compounds, so degradation cannot be determinate by FT-IR. Although spectrum has not change, it does not mean there is no degradation of the fatty acids. Some reactions such as ramification or polymerisation could be happening and infrared spectroscopy would not detect because there are not new functional groups after the degradation.

Myristic acid after 500 hours shows a different spectrum, with a wide peak at 3500 cm^{-1} to 3000 cm^{-1} which belongs to the O-H stretching from the water, because this sample was wet after the thermal treatment.

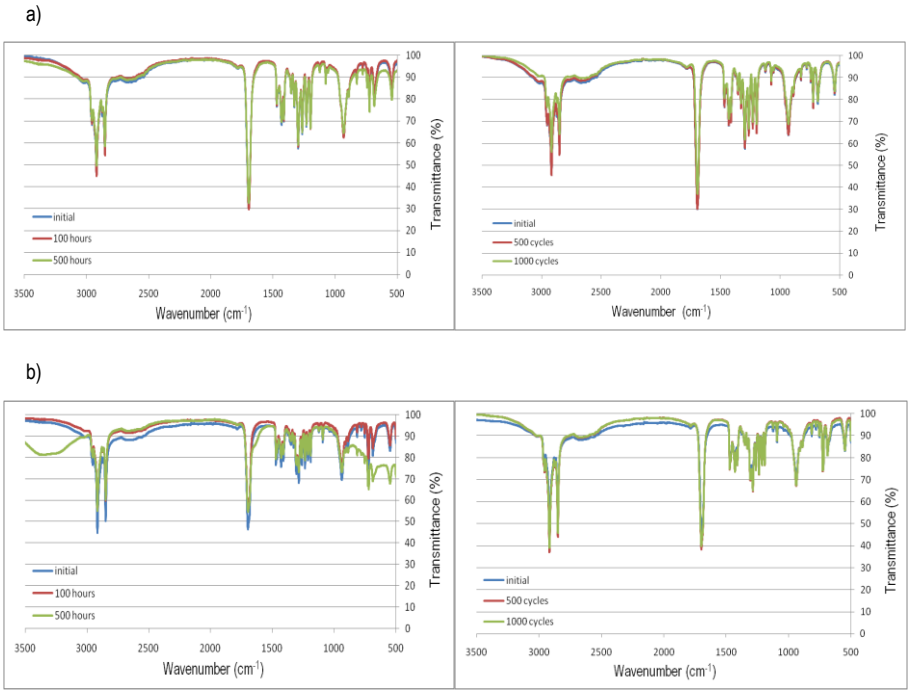


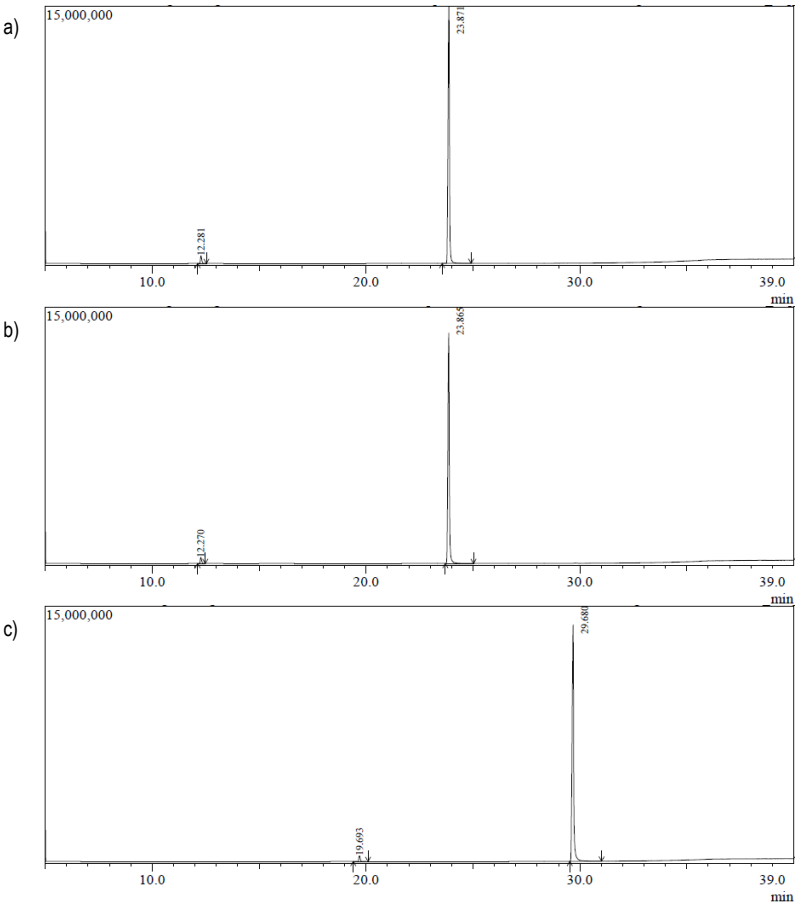
Figure 8. FT-IR results: a) capric acid b) myristic acid

Gas Chromatography

This is the most transcendent technique of the characterisation in this project because allow to detect different compounds of every sample, and analyse their structure with the help of the

mass spectrometer. Two or more peaks in the chromatograph will mean there is more than one substance in the sample, and that fatty acids must be degraded during the thermal treatments.

As it can be observed in Figure 9, chromatography confirms the initial hypothesis of a degradation of fatty acids after thermal treatments. The chromatographs show an intense peak at 23,9 minutes in the case of capric acid, and at 29,7 minutes for the myristic acid. However, there also appear new peaks for both fatty acids and both treatments at lower retention times.



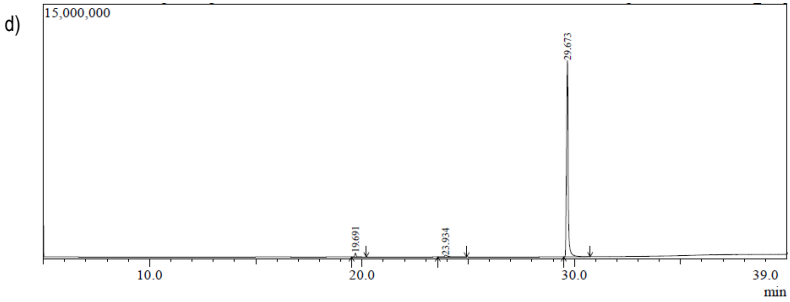


Figure 9. Chromatographs: a) Capric acid 500 hours b) Capric acid 1000 cycles c) Myristic acid 500 hours d) Myristic acid 1000 cycles

In the capric acid chromatographs a new peak appears at 12,3 minutes (Table 6). This new signal can be seen in samples treated with the thermal stability and cycling stability treatments, so the degradation product is the same. The intensity of the signal, corresponding to the area of the peak, is low because only a part of the capric acid has been degraded. Further exposition to the experiments should lead to a higher degradation of the fatty acid, and higher intensity of the new peak, even the apparition of new products. This lower signal has been detected and identified by the mass spectrometer as methyl decanoate, the methyl ester resulting of the capric acid.

Same reaction can be observed in myristic acid, being methyl myristoate the degradation product at a retention time 19,7 minutes, also the methyl ester of the initial fatty acid. Despite the chromatographs corresponding to the cycling stability treatment in myristic acid also reveals a third peak at 23,9 minutes, this signal appears due to a contamination of the sample with capric acid.

Sample	Treatment	Nº hours/cycles	Tr [min]	Area [%]
Capric acid	Thermal stability	100	23,9	100
		500	12,3	2,5
			23,9	97,5
	Cycling stability	500	12,3	1,3
			23,9	98,7
		1000	12,3	2,3
			23,9	97,7
Myristic acid	Thermal stability	100	19,7	1,7
			29,7	98,3
		500	19,7	2,0
			29,7	98,0
	Cycling stability	500	19,7	2,4
			23,9	1,3
			29,7	96,3
		1000	19,7	1,4
			23,9	1,5
			29,7	97,1

Table 6. Gas chromatography numerical results

7. CONCLUSIONS

The main objective of this project was to evaluate if capric acid and myristic acid, as representative substances of fatty acids used as PCM in buildings, degrade after thermal treatments which simulate daily conditions. At this point, it is confirmed that fatty acids degrade after this kind of treatments, and their first degradation product for capric acid and myristic acid are their respective methyl ester.

As expected, FT-IR has not been relevant for the structural characterization, and degradation cannot be determinate with this analytical technique. However, gas chromatography with mass spectroscopy as detector has played a key role in the characterization, allowing to detect and to identify the products resulting from the degradation of both fatty acids.

Rheological measurements have not been as significant as firstly though because viscosity only changed in one of the samples, making these results not conclusive.

On the other hand, DSC shows a decrease in thermo-physical properties such as melting point and melting enthalpy. This behaviour towards thermal treatments, confirms that degradation of fatty acids used as PCM, directly affects to the efficiency of the TES system, making them less efficient. Moreover, the maximum working temperature is 100 ºC for capric acid and 135 ºC for myristic acid.

In general terms, regarding the most relevant properties to apply the fatty acids as PCM in buildings, the reduction of thermal energy storage capacity measured by DSC (phase change enthalpy), was quantified as 7% for capric acid and 9% for myristic acid. This is still not stable because after 500 hours thermal treatment and 1000 thermal cycles, this property does not achieve the steady state conditions. Therefore, further research is required and I suggest performing at least 2000 hours thermal treatment and 3650 thermal cycles that corresponds to 10 year in service.

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9. ACRONYMS

TES: Thermal energy storage

SHTES: Sensible heat thermal energy storage

LHTES: Latent heat thermal energy storage

PCM: Phase change material

TCTES: Thermo-chemical thermal energy storage

LTS: Long-term stability

FT-IR: Fourier transform infrared spectroscopy

TGA: Thermo-gravimetric analysis

ATR: Attenuated total reflectance

DSC: Differential scanning calorimetry