CONFERENCE PROCEEDINGS

13th National and 4th International Conference in Engineering Thermodynamics

-

13er Congreso Nacional y 4º Congreso Internacional de Ingeniería Termodinámica

Advances in Engineering Thermodynamics: The Key to Sustainable Development
Avances en Ingeniería Termodinámica, la clave de un desarrollo sostenible

Jaume I University, Castellón, Spain
Universidad Jaume I, Castellón, España

November 29th, 30th and December 1st, 2023

EDITORS: Ramón Cabello, Rodrigo Llopis, Daniel Sánchez; Laura Nebot-Andrés
Universitat Jaume I, Spain

ISBN: 978-84-09-52403-7

13CNIT-ID815

Study of crystallization and melting-solidification processes in some fatty acids as phase change materials (PCMs)

Alejandro Peña-Tapia[1], Gabriel Rubio-Pérez[1], Raúl Briones-Llorente[1], Miriam Lorenzo-Bañuelos[1], Mohamed Lifi[2], Fernando Aguilar[1], Natalia Muñoz-Rujas[1,*]

[1]Departamento de Ingeniería Electromecánica, Escuela Politécnica Superior, Universidad de Burgos, Avenida Cantabria s/n, Burgos, Spain, Phone: +34-947258916

[2]Grupo de Ingeniería, Economía y Dinámica de Sistemas (GEEDS), Universidad de Valladolid, Valladolid, Spain, Paseo del Cauce, Phone: +34-983184798

* nmrujas@ubu.es

1. Introduction

The awareness on environmental problems has led to the increase in the use of renewable energy resources. Following this line, the program Horizon Europe [1], which has to be developed during the period 2021-2027, will be a key instrument to promote their worldwide development, taking special attention to the actions that fight the climate change and incentive a responsible use of the energy, specially setting the spotlight on renewable resources.

Nevertheless, the use of renewable energy resources depends on the problem of the temporality of the climate: solar, wind, geothermal energies, among others, are not always equally available over time. This means that sometimes the energy demand of the user doesn't match the availability of the renewable energy resource. In that case, it is necessary to use energy storage systems to satisfy the energy demand during the whole day. Thermal Energy Storage Systems (TES) involve the energy storage either by the heating or cooling of a fluid (sensible heat), or using the phase change of a material (latent heat).

In some cases, the use of systems that employ renewable energy resources, as happens with conventional energy resources, implies that a part of the energy is dissipated as heat, which is in most on the cases non desirable. This phenomenon can also lead to the failure of the systems by overheating, such as in the case of electric vehicle batteries, electric machines, or electronic components. In this case, it is also desirable to use materials capable of absorbing this heat. The fact of using the phase change of different materials allows the process of heat transfer to take place at the same temperature. This is especially important when working with heat pumps, for example, because the energy exchange at constant temperature increases the seasonal efficiency of the pump.

Focusing on the materials that could be used to this purpose, Phase Change Materials (PCMs) cover a wide range of possibilities. Many substances have been investigated as PCMs. Some papers [2,3] present several inorganic and organic materials as well as mixtures that have been studied as potential PCMs, depending on the phase change temperature, its energy properties and safety characteristics. Only some of these PCMs are sold in the market, being mainly hydrated salts and organic paraffins. Since some years ago, a new kind of PCMs, the so-called bio-PCMs are being developed. These bio-PCMs come from renewable resources, such as vegetable oils and recyclable waste, and cover different materials, being some of them fatty acids and esters.

Generally, commercial PCMs and bio-PCMs are sold encapsulated in plastic materials (cylinders, spheres, rectangular blocks, etc), that are able to absorb the volume variation of the PCM during the phase change.

Although these materials are used nowadays, not much knowledge is available concerning their thermophysical properties. This is the case of the lack of knowledge of the volume change during the phase change, and the temporal distribution in which the solid-liquid phase transition takes place. The consequence of this implies that the energy exchange process carried out by the PCM in the devices that use them is not properly modelled. This creates inefficiencies that reduce the expected potential improvement. In the same way, the change in the cooling velocity involves the formation of crystals of different shape, with preferent directions, which could affect largely the functionality of the installation.

This paper gathers the study of the melting-solidification processes, as well as the crystallization, of two pure fatty acids and their eutectic mixture, that can be used as bio-PCMs in renewable energy storage applications by means of latent heat at low temperature.

Melting-solidification processes and supercooling effects have been studied, determining the phase change velocities depending on the temperature interval considered. Furthermore, the process of crystallization during solidification depending on the phase change velocity has been determined.

2. Materials and methods

The two pure bio-PCMs used in this work are two fatty acids: capric acid and lauric acid. Capric acid (CA) is another name for decanoic acid, and lauric acid (LA) is another name for dodecanoic acid. Both of them are mainly obtained from palm and coconut oils. The two PCMs have a mass purity ≥98%, and they have been purchased from Sigma-Aldrich. The eutectic mixture of these two compounds has also been employed for the experiments. The formulae, mole compositions and melting-solidification temperatures of the three PCMs are gathered in Table 1. The melting-solidification temperatures of these components make them

suitable to be used in low-temperature energy storage applications. These values have been obtained by measuring them with a NETZSCH (model DSC Polyma 214) apparatus. The measuring procedure and the values obtained are covered in reference [4].

The eutectic mixture has been obtained by mixing the two pure components, weighing the appropriate amounts of each one to reach the mole composition shown in Table 1.

Table 1. Fatty acids used as bio-PCMs in this study and their melting-solidification temperatures.

Compound	Formula	Mole Composition CA (x)	Melting-Solidification Temperatures (ºC)
Lauric Acid (LA)	$CH_3(CH_2)_{10}COOH$	0	40.99 - 43.18 [4]
Capric Acid (CA)	$CH_3(CH2)_8COOH$	1	27.52 - 30.33 [4]
Eutectic Mixture (CA+LA)	-	0.7513	17.72 - 18.84 [4]

The experimental device used to determine the melting-solidification processes, as well the crystallization of the three samples, consists of a cylindric measuring cell made of stainless steel, with both sides made of borosilicate glass, in order to allow the visualization of the process and the introduction of the sample. The temperature control to let the sample melt or solidify is carried out by means of an external cooling bath from the brand Julabo, model Corio 201F. This construction of the whole device provides two main characteristics.

the first one allows the control of the melting or solidification velocity. This velocity is responsible for the change in the melting-solidification temperatures, being this the reason for which more than one value is available for the phase change temperature. The cooling velocity in this kind of materials is of great importance, because it is affected by the supercooling phenomenon, which can be defined as the lowering of the temperature of the sample below the solidification temperature, without the sample reaching solid state.

The second characteristic is that the device is made with two different geometries, allowing the study of the crystallization considering different geometries of containers.

The design of the device is conceived to be used principally with phase change materials as fatty acids and esters with a range of phase change temperatures between 15ºC and 50ºC. This means that the materials that could be studied are mainly used in low-medium temperature applications.

To obtain videos and pictures of the different stages of the experiments, a smartphone Samsung model Galaxy S8 has been used.

To conduct the experiments, a beaker is filled with an amount of the pure component or the eutectic mixture, up to a height of 1 cm approximately. This allows a better visualization of the crystallization process, as well as a better determination of the volume change between melting and solidification by measuring the change in height. Two different kinds of experiments can be conducted. In the first one, the material is initially in liquid state, to study the solidification process. To reach the liquid state, a Fisherbrand incubator has been used. Once introduced in the visualization device, the temperature that must be reached is programmed in the cooling bath, letting the material solidify. In the second kind of experiments, the material is introduced in the visualization device in solid state. Then, the bath is programmed to increase the temperature to let the material melt up to the set point.

3. Results and discussion

Melting and solidification processes have been studied in the three compounds. The time needed to reach the phase change, that is, the cooling or warming rate, the experienced temperature change, and the average size of the crystals obtained in the solidification processes are gathered in Table 2.

For pure capric acid (CA), one experiment for melting and three for solidification have been conducted. In the case of the solidification, the three experiments have reported a temperature change from 35.0ºC to 27.0ºC, 28.0ºC and 29.0ºC, respectively, to reach the exact temperature at which the component solidifies. Depending on the time needed to solidify, the size of the crystals obtained has varied from 1.5 to 3.0 cm. As can be extracted from Table 2, the lower the cooling rate needed to solidify is, the higher the size of the crystals obtained is. To determine the volume change of the sample, the average value of change in height of the sample obtained during melting-solidification processes has been of 0.5 mm. Fig. 1 shows some pictures taken during the melting and solidification experiments for capric acid.

In the case of pure lauric acid (LA), one melting experiment and one solidification experiment have been carried out. In both experiments the temperature change has been similar, being the crystal size obtained in the solidification of 0.5 cm approximately. It must be noted that, to reach the solidification of the material, the temperature has had to be reduced quite below the reported solidification temperature due to the phenomenon of supercooling. The change in height observed during the solidification has not been noticeable. In Fig. 2 certain steps of the melting-solidification processes can be seen.

Due to the importance in the different potential applications of the eutectic mixture due to its phase change temperature, more melting-solidification processes have been studied with it to well characterize the processes. A total of five melting and five solidification experiments have been conducted, employing different time periods (from 5 h to 24 h) and several temperature changes. Concerning the shape of the crystals formed during the solidification, all cases have shown a snowflake shape, with a size change of 0.4 to 0.6 cm. The average change in height observed has been of 0.2 cm, which means a small change in volume during

solidification. This is congruent with the values obtained for the two pure components, in which the height change has been higher and lower respectively. Fig. 3 shows different stages of melting and solidification for the eutectic mixture during different experiments.

Table 2. Melting-solidification characteristics for the three compounds studied. (-) means "not determined".

Pure Capric Acid (CA)			
Process	Temperature change (ºC)	Time needed to reach phase change (h)	Crystals size (cm)
Melting	19.5 to 35.0	±5.0	-
Solidification	35.0 to 27.0	±7.0	1.5
	35.0 to 28.0	±7.0	2.0
	35.0 to 29.0	±7.0	3.0
Pure Lauric Acid (LA)			
Process	Temperature Change	Time needed (h)	Crystals size (cm)
Melting	25.0 to 44.0	±5.0	-
Solidification	46.0 to 31.0	±7.0	0.5
Eutectic Mixture (CA+LA)			
Process	Temperature Change	Time needed (h)	Crystals size (cm)
Melting	12.0 to 20.0	±24.0	-
	19.0 to 25.0	±8.0	-
	12.0 to 20.0	-	-
	5.0 to 18.0	±5.0	-
	16.0 to 30.0	±5.0	-
Solidification	25.0 to 12.0	±5.0	0.5
	27.0 to 12.0	±4.0	0.4
	18.43 (ambient) to 5.0	-	0.5
	25.0 to 5.0	±8.0	0.6
	30.0 to 7.0	±5.0	0.5

In all cases, during melting and solidification processes, convective flow has been observed. It is remarkable the appearance of air bubbles inside the sample of lauric acid, that had been trapped in the solid after the phase change. During the solidification, the nucleation has taken place from the outside to the inside, since the outer part of the beaker has been in contact with the steel cylinder of the device, which has been in turn in contact with the cold water used to decrease the temperature.

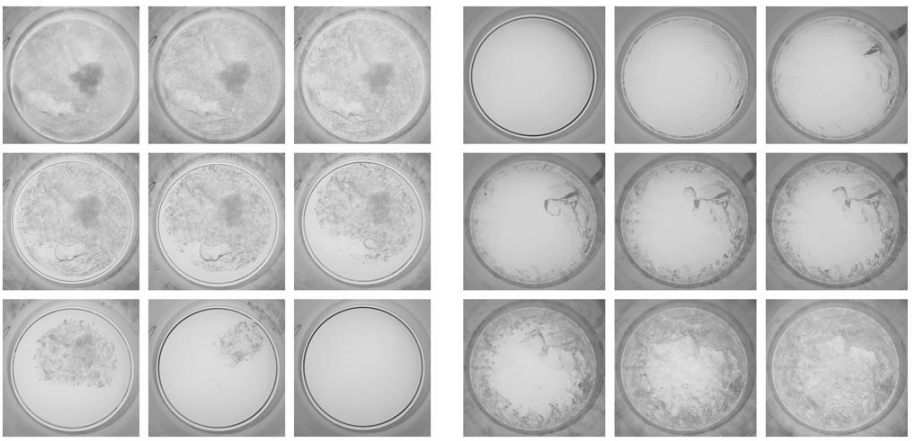

Fig. 1. Left picture: Melting process for capric acid. Right picture: Solidification process for capric acid.

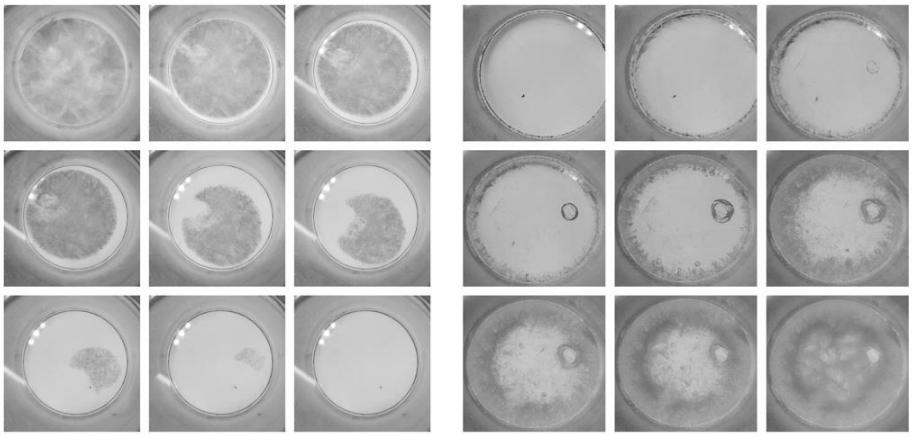

Fig. 2. Left picture: Melting process for lauric acid. Right picture Solidification process for lauric acid.

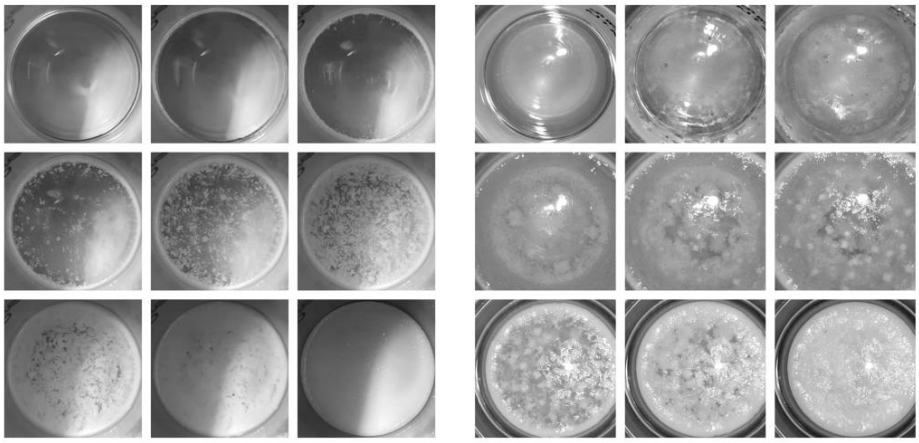

Fig. 3. Left picture: Melting process for the eutectic mixture. Right picture: Solidification process for the eutectic mixture.

4. Conclusions

Due to the necessity of knowledge concerning the melting-solidification processes in phase change materials and, in order to apply it to real installations, the phase change of two pure fatty acids, capric acid (CA) and lauric acid (LA), as well as their eutectic mixture (CA + LA) has been studied. A visualization device coupled with a thermostatic bath has allowed the determination of the melting and solidification processes between a range of temperatures, obtaining the time needed to reach the phase change. In the same way, the characterization of the size of the crystals obtained, and the change in the height of the sample during the solidification, has been determined. In the case of capric acid, the most remarkable event is the change in the size of the crystals when changing the velocity of solidification. The lower the speed of solidification is, the higher the size of the crystals obtained. Moreover, the phenomenon of supercooling has been observed in this material. It can be also remarked that the size of the crystals is proportional to the subcooling experienced in the PCM. For lauric acid, only one experiment for melting and one for solidification have been carried out. It is worth mentioning that the change in the height of the material during solidification is practically inexistent. For the eutectic mixture, five melting and five solidification experiments have been conducted, considering different temperature windows and different changes in time to reach the phase change. In this case, the size of the crystals varies from 0.4 to 0.6 cm, whereas the change in height is in average 0.2 cm.

5. References

[1] Horizon Europe. https://www.horizonteeuropa.es (last accessed: 29/06/2023).
[2] Zalba, B., et al., Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. Applied Thermal Engineering, 2003. 23: p. 251-283.
[3] Cabeza, L. F., et al., Materials used as PCM in thermal energy storage in buildings: A review. Renewable and Sustainable Energy Reviews, 2011. 15: p. 1675-1695.
[4] Rubio-Pérez, G., et al., Calorimetric properties of binary mixtures decanoic + dodecanoic acids as phase change materials. XI Congreso Nacional y II Internacional de Ingeniería Termodinámica, 2019, Albacete, Spain.