

# Thermal performance enhancement of organic phase change materials using spent diatomite from the palm oil bleaching process as support

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## HIGHLIGHTS

- A PCM from palm oil industry waste have been elaborated.
- The study include PCM base from raw, recycled, and recycled-calcined diatomite.
- The results show the effectiveness of the use of recycled-calcined diatomite.
- PCM was characterized by DSC, TGA, FT-IR and SEM.
- The PCM have potential applications in thermal energy storage in buildings.

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## ABSTRACT

This paper presents a sustainable PCM for potential applications in thermal energy storage in buildings. Up to date, PCMs are elaborated with raw and expensive materials. Therefore, the main appeal of the PCM is its support material, recycled diatomite, a palm oil industrial waste. PCMs were elaborated with three support materials (raw, recycled, and recycled-calcined diatomite) to compare its influence on PCM thermal and chemical behavior. Different mixtures of organic components (esters of palm oil and commercial stearic acid in different proportions) were incorporated into the three support materials. A characterization process by differential scanning calorimetry (DSC) was used to select the organic mixture with the highest value of latent heat of fusion and the closest phase change temperature range to the thermal comfort in each support material. To establish the thermal and chemical stability of the PCMs, DSC, thermogravimetry (TGA), and Fourier-transform infrared spectroscopy (FT-IR) analysis were carried out at 0, 120, 240 and 360 thermal cycles. One of the major outcomes from these joint efforts is the good and long thermal and chemical performance of the PCMs composed by 100% of commercial stearic acid methyl esters and recycled-calcined diatomite. This PCM is capable to have a similar energy storage capacity to the PCM supported in raw diatomite. The results show the effectiveness of the use of recycled-calcined diatomite as support material to obtain potential and sustainable PCMs for energy saving.

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## 1. Introduction

The energy demand required to maintain thermal comfort in buildings has grown continuously in the last years, among other

reasons, due to an increasing number of users and consequently, a growing demand of mechanical air conditioning systems in the market [1,2]. The energy required for the operation of air conditioning systems is mainly sourced from fossil fuels, whose use increase the level of greenhouse gas emissions and the climate change [3,4].

Thermal storage, a well-known technology within the framework of renewable energy, can reduce the negative impact produced by the utilization of energy associated to air conditioning systems in buildings [5]. The latent heat of a material can store

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5–10 times more energy than its sensible heat [6,7]. During heating-cooling stages, PCMs undergo a physical transformation known as fusion-solidification cycle, which is completely reversible [8]. This two phase transformation process consists of: (1) the melting process, where material absorbs energy from the surroundings while remaining at a constant temperature, and (2) the solidification process, where the stored energy is delivered to the surroundings.

The energy absorbed and released at constant temperature during the fusion-solidification cycle, can be used to reduce and/or substitute the energy demand associated to mechanical heating and cooling processes in buildings while maintaining thermal comfort [9]. So far, materials that present phase change temperature ranges close to thermal comfort range (18–30 °C) and high values of heat of fusion have been used in energy efficiency application in buildings [4,10,11].

An important factor in determining the performance of a PCM is the analysis of its stability over time. For this purpose, temperature conditions are simulated to allow the material reaches both its melting point and its solidification point. After the application of these heating and cooling cycles, their chemical and thermal stability are evaluated [12]. The chemical and thermal stability of a PCM are evidenced when its chemical structure and thermal properties (i.e. latent heat of fusion and temperature range of phase change) do not present changes after the application of thermal cycles. In addition, the thermal stability also refers to the fact that the material does not decompose in the temperature range in which it is going to operate [13].

In recent years, various organic and inorganic materials have emerged as potential PCMs for application in buildings [7]. Commercially available PCMs for such applications include inorganic salts and non-biodegradable paraffins (hydrocarbons); however, their cost and availability for large scale applications are major barriers for their use [9,14]. Organic PCMs show some advantages over inorganic ones. In particular, non-toxicity, better thermal properties and long-term thermal reliability under the application of several heating-cooling cycles [15].

Paraffins are by far the most studied organic PCMs [7]. However, such PCMs do not come from renewable sources and their use requires a deeper understanding of their carbon footprint and associated environmental impact [13,16,17]. A green organic alternative are fatty acid esters. This type of PCMs displays good chemical stability, they are non-toxic, and non-corrosive [18]. In particular, Xu et al. [13] determined that methyl stearate and methyl palmitate mixtures, which can be sourced renewably from palm oil, have a great potential as PCMs for buildings. Indeed, palm oil composition includes 32–48% of palmitic acid, 36–53% of oleic acid, 6–12% of linoleic acid, 3–6% stearic acid, among the main fatty acids [19,20]. Despite the potential applications of organic materials as PCMs, their energy storage capacity is lower than commercial hydrocarbon-based PCM capacity [6]. However, the use of nucleation agents that induce a crystallization of the organic components could increase heat transfer and improve the storage characteristics of organic PCMs [21,22,23].

In general, PCMs are encapsulated in porous materials, fibers and polymeric micro and macro capsules, to retain their liquid phase during the melting process [13]. The use of polymeric matrices for PCMs encapsulation generates free spaces during fusion-solidification processes that create heat transfer resistance [8,9]. In addition, several investigations have been reported in previous works on PCMs supported in porous materials [1,11,15,24,25,26]. These materials remain solid even when the melting point is reached at the phase change. According to Fleischer [9], supported PCMs present higher specific heat and latent heat for the phase transition temperature region and higher thermal conductivity, compared to the encapsulated PCMs. Moreover, PCMs stabilized

in porous supports do not require containers, and unlike encapsulated PCMs, the volume of the material does not change [25]. Jeong et al. [1] determined that the incorporation of PCMs in porous materials, using vacuum, allows improving the thermal properties of the PCMs and achieving a better impregnation of the organic phase in the porous surface of the material. These advantages make these types of PCMs potential energy storage materials for use in buildings [1,11,24].

Diatomite or diatomaceous earth is an amorphous siliceous mineral with distinctive properties; including a structure of high porosity (80–90%), thermostability, low density, high purity, excellent absorption capacity, is chemically inert and relatively low cost [1]. These properties allow the use of diatomite as a PCM support material [25,27]. At this time, diatomite is used in the discoloration or bleaching of edible oils due to its ability to absorb dissolved dyes, phosphatides, fatty acids, gums, traces of metals, etc. [28,29]. However, diatomite is used only once during vegetable oil bleaching, and it is usually landfilled. Consequently, its final disposition can be a potential source of soil pollution and represents an economic cost [29,30]. Alternatives to the final disposition of spent diatomite, such as thermal or solvent regeneration, incineration, brick and block production and bio digestion, need to be considered [29]. Regarding regeneration of spent diatomite, it can be achieved through thermal processes, extraction with solvents or a combination of both [29]. Thermal treatments for regenerating used or spent diatomite, temperatures above 600 °C should be used to ensure organics removal [30].

Extensive studies have been focused in organic PCMs supported in porous materials. Those studies presented organic PCMs supported in porous materials with latent heat of fusion between 35 and 119 J/g and phase change temperatures of 16.7 and 31.8 °C [8]. Nevertheless, neither of the above studies have used recycled materials as support material for PCMs. Additionally, it should be emphasized that no information is available on the use of diatomite from the oil bleaching process as a support material for the elaboration of phase change materials. In this sense, the present study aims to provide initial information on the development of sustainable phase change materials (PCMs) from palm oil extraction industry residues, which currently have no economic value.

In the context of sustainable phase change materials, this study answered a fundamental question:

How can the use of recycled diatomite as a support material improve the chemical and thermal behavior of a sustainable PCM?

To answer this question, organic esters supported in recycled-calcined diatomite were prepared, and its chemical and thermal properties were compared with PCMs supported in raw diatomite and non-treated recycled diatomite. To determine its main chemical and thermal characteristics, the PCMs were characterized through several techniques such including differential scanning calorimetry (DSC), thermogravimetry (TGA), Fourier-transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM).

## 2. Material and methods

### 2.1. Materials

In the present work, PCMs composed of a support material and an organic phase were prepared and studied. As support material for the PCMs, new, spent (diatomite from the bleaching process of crude palm oil), and recycled-calcined diatomite with a D90 of 90  $\mu\text{m}$  were used. The porosity of the new diatomite was 65%. As the organic phase, mixtures of palm oil, overproduced raw material in Ecuador, and commercial stearic acid, cheap by-product of the

palm oil production process, esters were used in different proportions (100–0, 75–25, 50–50, 25–75, 0–100%) (w/w).

The crude palm oil and the spent diatomite that were used in the present investigation were obtained from an oil extraction company in Ecuador.

## 2.2. Preparation of the PCMs

### 2.2.1. Characterization of palm oil and commercial stearic acid

The characterization of palm oil and commercial stearic acid consisted of the fatty acids quantification. For this purpose, gas chromatography analyzes were performed on a Perkin Elmer Clarus 500 chromatograph. Extra pure helium 5.0 was used as the carrier gas [31]. In addition, two analyzes were performed in rapid succession for each sample, until the obtained error was less than 5% [32].

### 2.2.2. Preparation of palm oil and commercial stearic acid esters

For the preparation of esters of crude palm oil and commercial stearic acid, conventional trans esterification was carried out with methanol. For this purpose, sulfuric acid ( $H_2SO_4$ ) was used as catalyst and 2% w/w was added with respect to the mass of reactants. A fatty acid/methanol molar ratio of 1:10 was used. The process was carried out at 55.0 °C and for 5 h. For the purification, the product obtained was washed with water and then with ethyl ether [33].

### 2.2.3. Characterization of esters of palm oil and stearic acid

Esters of both palm oil and commercial stearic acid were characterized by gas chromatography and DSC. To determine qualitatively and quantitatively the composition of the esters a Perkin Elmer gas chromatograph was used. Sample preparation consisted of a 2000 ppm dilution with petroleum ether and then passed through a Millipore Millex-HV 0.45  $\mu m$  filter [34].

On the other hand, the esters were characterized by DSC in a Q 2000 1714, TA Instruments apparatus. The phase change temperature and latent heat of fusion were determined for each one of the obtained esters. Measurements were carried out at 0–60 °C with a heating rate of 4 °C/min under an inert atmosphere of nitrogen with a flow rate of 20 mL/min [13]. The phase change temperature range considered was from T onset to T end determined by the equipment.

### 2.2.4. Characterization of spent diatomite

The spent diatomite was characterized by a proximal analysis that considered the determination of moisture, ash content, volatiles and fixed carbon in accordance with BS EN standards [37]. The moisture content was determined by gravimetry based on BS EN 18134-1 standard [35]. The determination of volatile matter and ash content was carried out based on BS EN 15148 and BS EN 18122, respectively [35,36].

Additionally, the oil content in the spent diatomite was determined through solvent extraction [28]. After the extraction was complete, the sample was dried at 110 °C for 4 h. The amount of oil retained was determined by gravimetry.

### 2.2.5. Calcination of spent diatomite

Different calcination times (1 and 2 h) and temperatures (400, 550 and 700 °C) of the spent diatomite were studied. The conditions that allow to use a smaller amount of residual diatomite, and an impregnation of an equal amount of esters of fatty acids calcination treatment were selected. The calcination tests were carried out in triplicate ( $n = 3$ ). The response variable corresponded to the impregnation percentage of the organic esters in the recycled-calcined diatomite [25].

The results of the throw put were statistically analyzed, to find the time and temperature conditions of calcination that allow to take advantage of the use of the residual diatomite as support material of the PCMs.

### 2.2.6. Preparation of phase change materials (PCMs)

For the preparation of the PCMs, new, recycled, and recycled-calcined diatomite were used as support material for mixtures of palm oil and commercial stearic acid esters as the organic phase.

**2.2.6.1. Experimental design.** In order to determine the PCMs that have the most suitable thermal properties to store thermal energy in buildings, a completely randomized experimental design (DCA) was proposed for each type of support material. The factor studied was the ester proportion of palm oil and commercial stearic acid esters in five levels (100–0, 75–25, 50–50, 25–75, 0–100%) (w/w), respectively.

**2.2.6.2. Impregnation of the esters of palm oil and stearic acid in the support materials.** In order to obtain the PCMs, 10 g of the support material were put inside a flask, which was connected to a water trap and a vacuum pump, as indicated in Fig. 1; a vacuum pressure of 27 kPa was maintained for 30 min. The organic phase entered into the flask, and the same vacuum pressure was maintained for 90 min [1,17].

In order to determine the energy storage capacity of each prepared PCM, the latent heat of fusion was quantified in each case. For this, differential DSC scanning calorimetry analyzes were done in triplicate, under the same conditions as those mentioned in Section 2.2.3.

By using Statgraphics Centurion XVI statistical software, the PCM that had the highest latent heat of fusion and a phase change temperature range close to the temperature range of thermal comfort (18–30) °C was selected from each type of support material [10]. Once the materials with the characteristics described above were selected, their thermal and chemical stability was evaluated by the application of heating and cooling cycles.

## 2.3. Evaluation of the thermal cycle's effect

To establish the thermal and chemical stability of the selected PCMs, heating and cooling cycles (120, 240 and 360 cycles) were applied. The phase change materials selected in Section 2.2.6 were heated to the phase change temperature, and then cooled until its solidification temperature. For the heating of the PCMs, a stove was maintained at 50 °C. On the other hand, for the cooling process, a refrigerator was used which was maintained at 8 °C. These temperatures were selected to ensure that both melting and solidification temperatures were reached [12].

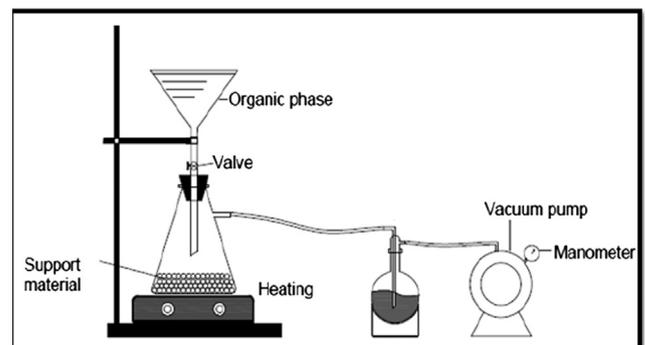


Fig. 1. Schematic representation of the vacuum impregnation process.

The thermal stability of the PCMs was analyzed by DSC under the same conditions detailed in Section 2.2.3 and by TGA in a Shimadzu equipment in a temperature range of 25–600 °C, with a heating rate of 10 °C/min and a nitrogen flow of 50 mL/min were carried out [1]. Moreover, chemical stability was analyzed by FT-IR Perkin Elmer, Frontier in a wavelength range of 4000–400 cm<sup>-1</sup>. The PCM chemical changes were studied by comparing the FT-IR analyses before and after the thermal cycles [1].

Additionally, to evaluate the morphology of the PCMs and the possible changes after the application of 120 thermal cycles, scanning electron microscopy (SEM) analysis were performed in a TESCAN Vega 3 microscope with a voltage of 20 kV [38].

By comparing the analysis described above, the most suitable PCMs for temperature regulation in buildings were determined according to their thermal and chemical stability [8].

### 3. Results and discussion

#### 3.1. Properties of the palm oil and stearic acid esters, and spent diatomite

The results of the fatty acid composition in palm oil and commercial stearic acid are presented in Table 1. As can be seen, trans-9 elaidic acid (trans configuration of oleic acid), palmitic acid and linoleic acid are the most abundant acids present in palm oil (95.82%). These results correspond to those presented by Melero et al. [20].

In addition, it can be observed that commercial stearic acid presents only 51.10% of pure stearic acid, this could be because the purification process of stearic acid requires substances such as acetone, acetonitrile and ethanol, which make the product more expensive [39]. Although commercial stearic acid did not exhibit high purity, its economic value is less than pure stearic acid; which would make it possible to obtain lower cost PCMs. Moreover, Table 1 shows the composition of methyl esters present in palm oil and commercial stearic acid after the esterification process. These results allowed to know the composition of the mixtures that were used as organic phase in the preparation of the PCMs.

Diatomite, used in the process of bleaching palm oil, has a moisture level of 3.26%; 55.68% ashes; 0.49% of fixed carbon and 40.67% of volatiles (26.16% of oil retained in its pores and 14.51% of impurities acquired in the process). According to O'Brien [41], these impurities correspond to phospholipids, carotenoids and trace metals.

In order to use the spent diatomite as a support material for PCMs, it was necessary to eliminate the moisture content and volatile matter in such a way as to avoid the decrease of the surface available to be occupied by the organic phase in the preparation of the PCMs [1,30].

##### 3.1.1. Thermal properties of the pure components

In Fig. 2, the DSC melting curves of the palm oil and commercial stearic acid esters are presented. It was found that the phase

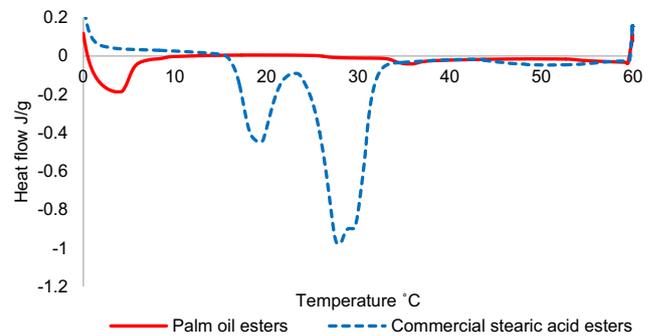


Fig. 2. DSC melting curves of the methyl ester of palm oil and the commercial stearic acid methyl ester.

change temperature range corresponds to 0.6–43.0 °C and 16.4–35.7 °C; and latent heat of fusion values of 13.86 J/g and 86.42 J/g, respectively. The value of the latent heat of fusion of palm oil esters was lower than the commercial stearic acid ones. The temperature range study did not include values such as the melting temperature of the trans-9 methyl elaidate (isomer of the methyl oleate) present in palm oil esters (–36 °C) [33]. This temperature was not considered because the temperature range of interest corresponded to values close to the thermal comfort temperature range.

##### 3.1.2. Calcination conditions

700 °C and 1 h were the best studied conditions for the spent diatomite calcination. Thermal regeneration treatments without a previous process of organic compounds extraction with solvents requires a temperature higher than 600 °C to eliminate the organic components retained in the spent diatomite pores. Furthermore, long periods of calcination time and temperatures above 500 °C and could decrease diatomite absorption capacity [29,30].

#### 3.2. Thermal properties of the PCMs

The nonlinear trend of the spent diatomite and the calcined was observed in Fig. 3. This trend could be attributed to the fact that the same amount of esters was not retained in the pores of the both support materials. The presence of palm oil, impurities and the decrease of the porous surface as a result of the heat treatment applied could be the causes [1,28]. Therefore, the amount of energy that PCMs can store depends on the amount of esters retained in the porous structures of the support materials, as well as the impurities they could present [41]. For that reason, while the content of the organic phase increase into the PCMs, the latent heat of fusion increase. In addition, the impurities that the spent diatomite presents cause the variation in the latent heat of fusion values.

Table 2 shows that the phase change temperature range is higher in palm oil esters than in commercial stearic acid esters, these results could be due to esterified palm oil is composed of

Table 1  
Composition of fatty acids present in crude palm oil and in commercial stearic acid and composition of methyl esters present in crude palm oil and commercial esterified stearic acid.

Fatty acids/methyl ester	Palm oil	Comercial stearic acid	Palm oil ester	Comercial stearic acid ester
Trans-9 Eláidico	43,61	0,00	50,17	0,00
Palmtic	36,78	48,18	20,03	49,20
Linoleic	15,43	0,00	15,80	0,00
Stearic	4,13	51,10	13,72	50,80
Caprilic	0,05	0,00	0,28	0,00
Miristic	0,00	0,72	0,00	0,00
Total	100,00	100,00	100,00	100,00

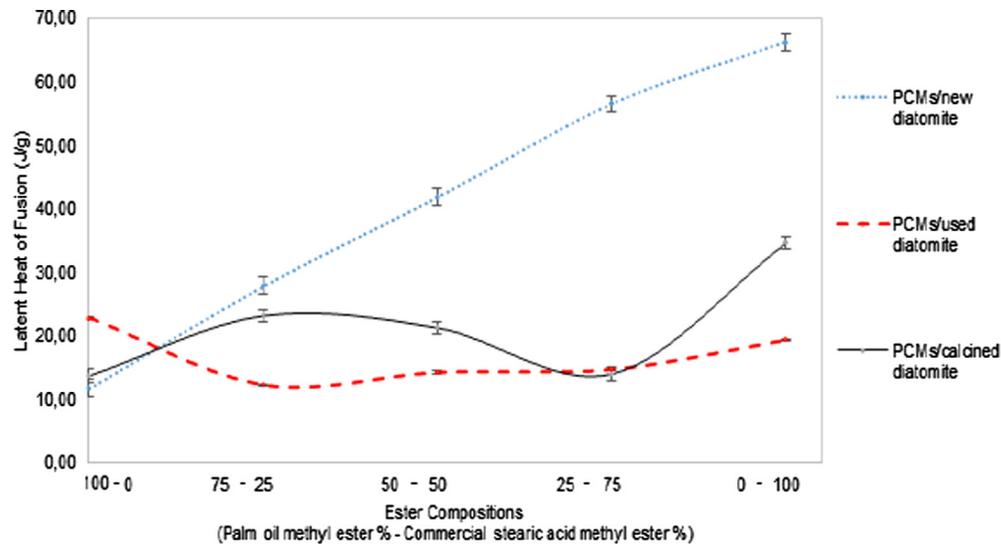


Fig. 3. Fisher's mean difference (LSD) for PCMs impregnated into new, spent and thermally treated diatomite.

**Table 2**  
Thermal properties of the PCMs.

Support material	Esters de P.O-esters de C.S.A composition (%-%)	T onset (°C)	T end (°C)	Latent heat of fusion (J/g)
New diatomite	100–0	0.9 ± 0.3	35.0 ± 1.3	11,8 ± 0.4
	75–25	10.8 ± 0.2	17.9 ± 1.5	27,9 ± 0.7
	50–50	2.2 ± 0.2	24.1 ± 1.5	41,9 ± 2.9
	25–75	19.2 ± 1.0	30.9 ± 0.7	56,5 ± 2.6
	0–100	17.5 ± 0.1	34.7 ± 1.1	66,3 ± 3.2
Spent diatomite	100–0	3.4 ± 0.4	26.3 ± 0.5	22,8 ± 0.0
	75–25	1.0 ± 0.7	42.5 ± 2.1	12,3 ± 0.2
	50–50	9.4 ± 0.7	41.3 ± 1.4	14,3 ± 0.3
	25–75	2.3 ± 0.6	25.0 ± 0.5	14,7 ± 0.4
	0–100	10.4 ± 0.1	25.7 ± 0.9	19,3 ± 0.2
Calcined diatomite	100–0	0.3 ± 0.1	36.2 ± 2.1	13,7 ± 0.2
	75–25	12.3 ± 0.7	26.3 ± 0.9	23,2 ± 2.9
	50–50	2.2 ± 0.3	21.3 ± 0.3	21,3 ± 0.4
	25–75	2.2 ± 0.4	16.9 ± 2.4	14,0 ± 0.5
	0–100	16.4 ± 0.4	33.5 ± 0.6	34,7 ± 2.6

P.O palm oil.

C.S.A commercial stearic acid.

different esters of fatty acids whose melting points range from  $-36^{\circ}\text{C}$  to  $39^{\circ}\text{C}$  [33]. The phase change temperature range decreases while the commercial stearic acid esters proportion increases. In the ester mixtures, while the quantity of commercial stearic acid esters increase the content of methyl palmitate and methyl stearate rise also, and 31 and  $39^{\circ}\text{C}$  are their phase change temperatures, respectively [13].

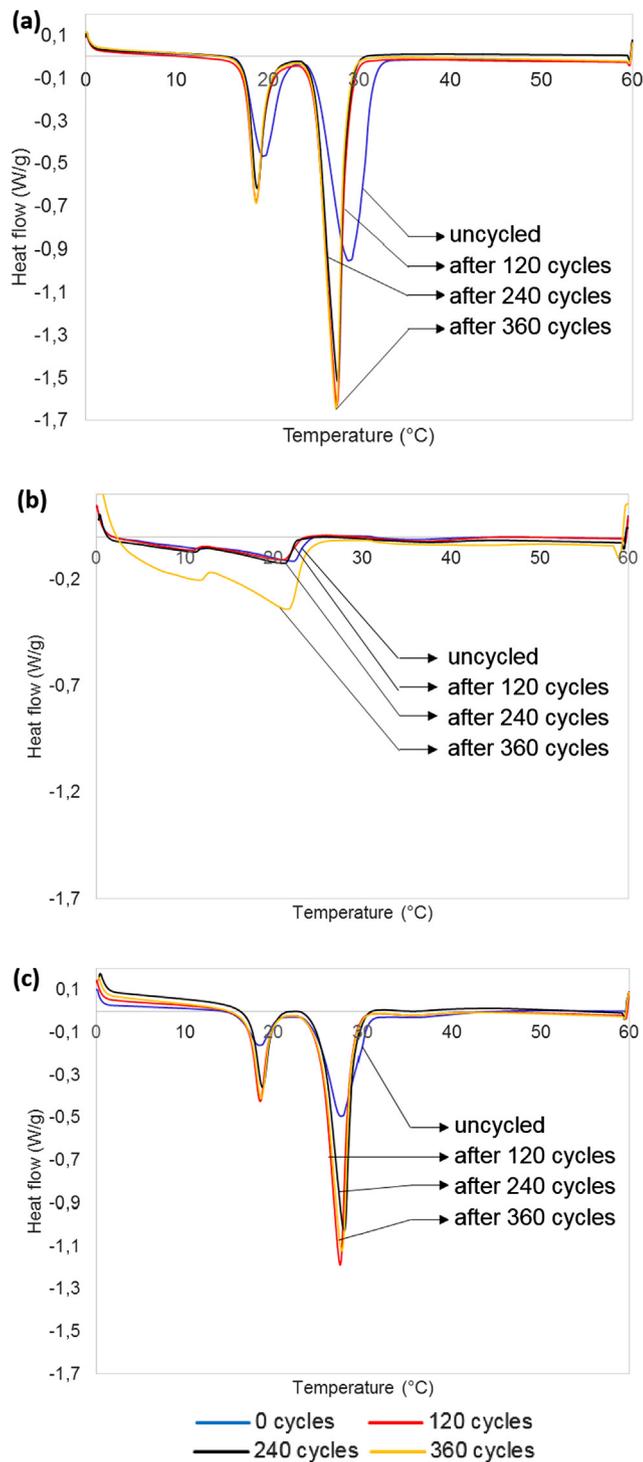
On the other hand, the latent heat of fusion is higher when 100% of methyl esters of commercial stearic acid are used for PCMs supported on new and calcined diatomite and when 100% of methyl esters of palm oil for PCMs supported on spent diatomite. However, as can be seen in Table 2, the phase change temperature range for spent diatomite does not coincide with the thermal comfort range. Therefore, its use would not be the most suitable in buildings [9,13]. Additionally, the PCMs, whose organic phase corresponds to 100% of commercial stearic acid esters and supported in each of the evaluated materials, were selected with latent heat of fusion of 66.3, 19.3 y 34.7 J/g, respectively. Those PCMs were selected because of their greater energy storage capacity [13].

### 3.3. Evaluation of the effect of thermal cycles

Heating and cooling cycles were applied to PCMs selected in Section 3.2 (100% commercial stearic acid) in order to evaluate the applicability of the PCMs as thermal energy storage systems. Thermal stability was analyzed by DSC and TGA analysis and the chemical stability by FT-IR analysis [12].

#### 3.3.1. Thermal analysis

The DSC curves of PCMs impregnated on new, spent and calcined diatomite are presented in Fig. 4A–C, respectively. After 360 thermal cycles, the area of the curve, the magnitude of the latent heat of fusion, present an increase [7]. Moreover, Table 3 shows the latent heat of fusion and temperature range of the PCMs after 0, 120, 240 and 360 thermal cycles. For the PCMs supported in new and calcined diatomite, the temperature range do not present a notable variation; however, when spent diatomite without thermal treatment is used, the values changed from  $16.7$  to  $31.1^{\circ}\text{C}$  to  $8.3$ – $26.8^{\circ}\text{C}$  before and after 360 cycles.



**Fig. 4.** DSC melting curves of PCMs supported in (a) new, (b) spent, (c) calcined, diatomite before and after the application of 0, 120, 240 and 360 thermal cycles, using 100% commercial stearic acid esters.

Additionally, the latent heat of fusion values changed in the three PCMs. For the new diatomite, the 360-cycle value changed from 62.05 to 73.02 J/g, from 21.32 to 26.25 J/g for the spent diatomite, and for the calcined diatomite from 30.12 to 53.57 J/g. As the values show, the latent heat of fusion value increase is almost double when recycled-calcined diatomite is used. This behavior could be explained by the fact that during the application of the thermal cycles the temperature conditions facilitated the crystallization process of the esters. This process produced an increase in the

**Table 3**

Thermal properties of 100% methyl esters of commercial stearic acid PCMs before and after 360 thermal cycles.

Support material	Thermal cycles	T onset (°C)	T end (°C)	Latent heat of fusion (J/g)
New diatomite	0	17.5	32.5	62.05
	120	17.4	32.1	76.54
	240	17.6	33.2	69.30
Spent diatomite	0	15.7	25.8	21.32
	120	6.4	46.8	24.48
	240	9.1	44.6	24.42
Calcined diatomite	0	8.3	26.8	26.25
	120	16.7	31.1	30.12
	120	17.2	31.8	54.26
240	17.3	33.2	51.41	
360	17.2	31.5	53.67	

latent heat of fusion of the evaluated PCMs [42]. The evaluated material can absorb a greater amount of energy because of the area increase, which enable the thermal comfort establishment in buildings [8].

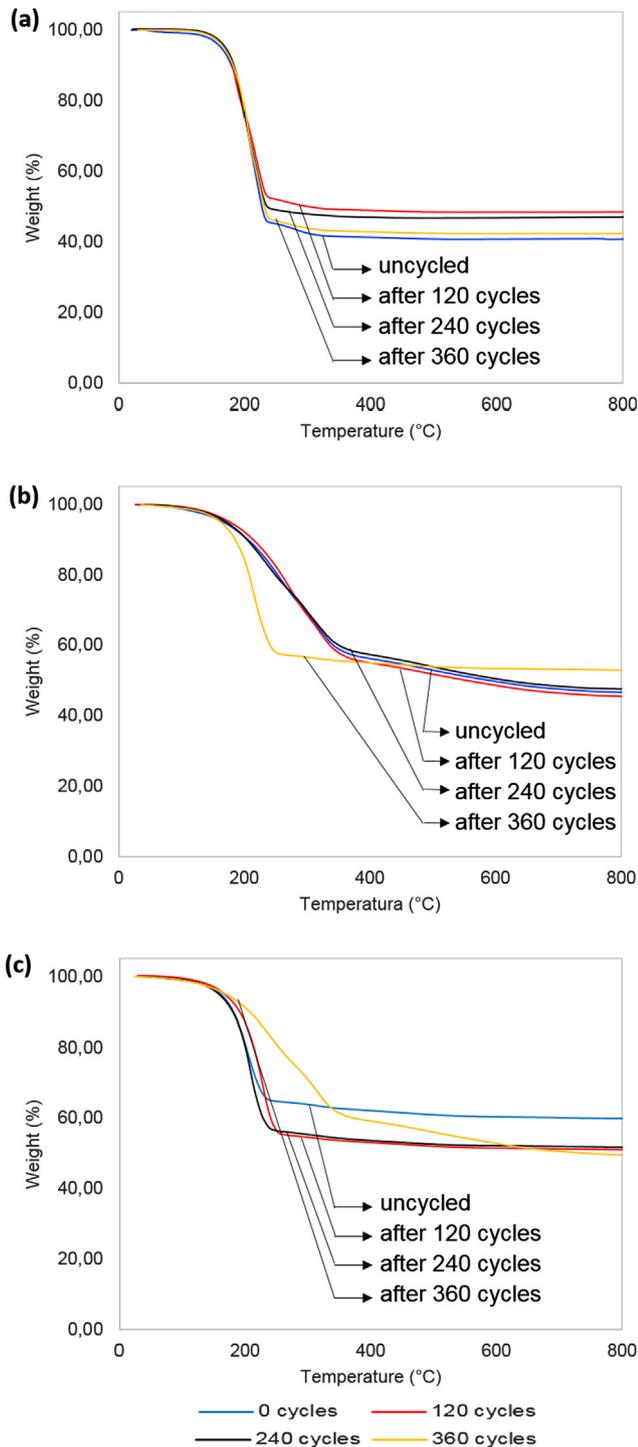
For PCMs impregnated in recycled-calcined diatomite, the increase in latent heat after the application of the 360 thermal cycles is 54.80% with respect to the initial value, as compared to the 10.19% and 35.73% that is evidenced in PCMs impregnated in new and spent diatomite, respectively. As shown in Fig. 4B, 360 cycles are required to increase the latent heat of fusion in the PCMs supported on spent diatomite; however, in the PCMs supported on new and recycled-calcined diatomite this increase was visible after the application of 120 cycles. This behavior could be attributed to the presence of fatty acids retained in the pores of the residual diatomite, since their thermal behavior differs from the others.

On the other hand, the variation in the melting temperature ranges are minimal for the three cases since the curves do not present horizontal displacement. However, to establish the cause of the increase in the latent heat of fusion, the changes in the chemical structures of the PCMs were analyzed by FT-IR [13]. The results of these analysis are presented in Figs. 6 and 7.

In Fig. 5A–C, thermogravimetric analyses determined that the PCMs do not present degradation at low temperatures. The loss of mass, when the PCMs were exposed to a heating from room temperature to 100 °C, is less than 2%. According to [7], this weight loss could be due to the loss of moisture present in the PCMs. However, as shown in Fig. 5B, after the application of 360 thermal cycles, the decomposition temperature of the PCM supported on spent diatomite decreases, this could be due to the fact that after the application of the thermal cycles, the decomposition of the components of the palm oil present in its pores was produced as indicated by [42]. This change in the thermal decomposition resistance corresponds to what is established in Fig. 4B, since a change in both the phase change temperature range and the latent heat of fusion value after the application of 360 cycles is evidenced.

In Fig. 5A it is not evident that the resistance to thermal degradation improved in the PCMs supported in new diatomite after the application of the thermal cycles. On the other hand, Fig. 5C shows that the PCM supported in calcined diatomite is degraded to higher temperatures after the application of 360 thermal cycles. It presents an improvement in its resistance to the thermal degradation. This result is corroborated by the improvement of the thermal properties observed in Fig. 4C and could be attributed to the rearrangement of the esters molecules and the formation of crystalline zones [42].

For the three cases evaluated by TGA it was evidenced that the organic phase do not released of the porous material; since at 100 °C which is a temperature higher than the phase change

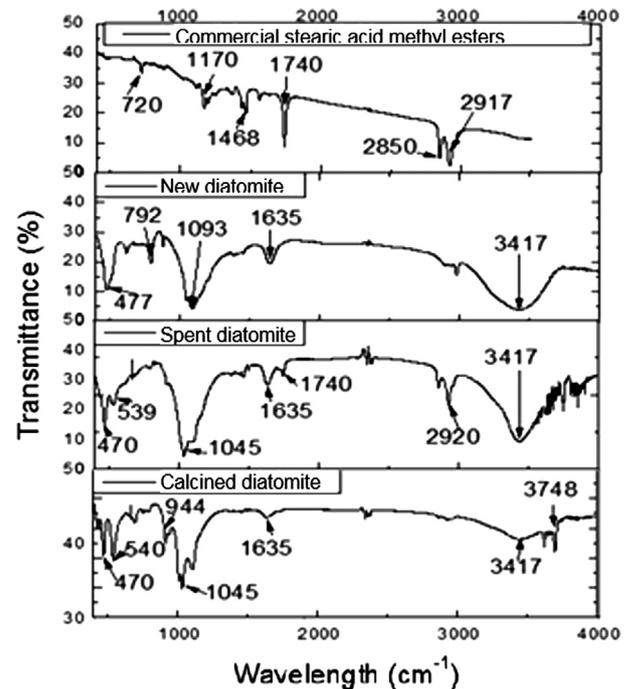


**Fig. 5.** Thermograms of PCMs supported in (a) new, (b) spent, (c) recycled-calcined diatomite before and after the application of 0, 120, 240 and 360 thermal cycles, using 100% commercial stearic acid esters.

temperature of the PCMs there is no loss of the organic phase [1]. This indicates that the analyzed PCMs are thermally stable and can be used as energy storage systems [15].

### 3.3.2. Chemical analysis

The FT-IR analyzes were performed in order to identify changes in the chemical structure of the PCMs due to the thermal cycles. In Fig. 6, the presence of  $-\text{CH}_2$ ,  $-\text{CH}_3$  groups and  $\text{C}-\text{O}$ ,  $\text{C}=\text{O}$  bonds of the esters of commercial stearic acid are observed, since by gas



**Fig. 6.** FT-IR spectrum of the organic phase and support materials used to make the PCMs.

chromatography it was determined that it consists of methyl stearate ( $\text{C}_{19}\text{H}_{38}\text{O}_2$ ) and methyl palmitate ( $\text{C}_{17}\text{H}_{34}\text{O}_2$ ). Peaks at  $720$  and  $1468\text{ cm}^{-1}$  were found which correspond to the symmetric and asymmetric vibration of the  $-\text{CH}_3$  group, respectively. In addition, the symmetric and asymmetric vibration of the  $-\text{CH}_2$  group is evident in the peaks present at  $2850$  and  $2917\text{ cm}^{-1}$ . The stretching vibration of the  $\text{C}=\text{O}$  group is evidenced at  $1740\text{ cm}^{-1}$  and the asymmetric vibration of  $\text{C}-\text{O}-\text{C}$  at  $1170\text{ cm}^{-1}$  [1].

On the other hand, the new, spent and calcined diatomite share peaks at  $1635\text{ cm}^{-1}$  and  $470-477\text{ cm}^{-1}$  corresponding to the vibration of the  $\text{O}-\text{H}$  group and the vibration of the  $\text{Si}-\text{O}$  group, respectively. In the new diatomite, a peak at  $792\text{ cm}^{-1}$  attributed to the  $\text{O}-\text{H}$  group is observed, the  $\text{Si}-\text{O}-\text{Si}$  vibration at  $1093\text{ cm}^{-1}$  and at  $3417\text{ cm}^{-1}$  the presence of the  $\text{Si}-\text{OH}$  group [8]. The spent and calcined diatomite share the following peaks at  $539-540\text{ cm}^{-1}$ ,  $1545\text{ cm}^{-1}$  and  $3417\text{ cm}^{-1}$  corresponding to the vibration of the  $\text{O}-\text{P}-\text{O}$ ,  $\text{Si}-\text{O}-\text{Si}$  and  $\text{Si}-\text{OH}$ , respectively [1,44]. The spent diatomite has peaks at  $1740\text{ cm}^{-1}$  and  $2920\text{ cm}^{-1}$  corresponding to the stretching vibration of the  $\text{C}=\text{O}$  group and the asymmetric vibration of the  $-\text{CH}_2$  group. The presence of this last peak is due to the 26.16% of residual palm oil that the diatomite contains in its pores, and the calcined diatomite does not present these peaks because the organic compound of the palm oil decomposes at temperatures above  $380\text{ }^\circ\text{C}$  [13,43]. On the other hand, the calcined diatomite has a peak at  $3748\text{ cm}^{-1}$  corresponding to  $\text{Si}-\text{OH}$  and at  $944\text{ cm}^{-1}$  the  $\text{Si}-\text{O}$  silanol stretching vibration [8]. Therefore it is observed that the three support materials have the proper bonds of a siliceous material such as diatomite [1].

In Fig. 7A and B, it is observed that the peaks of both new and calcined diatomite and the ester are maintained after the impregnation process. However, for the PCMs supported on spent diatomite, there are displacements of the peaks after the impregnation process. Particularly, from  $539\text{ cm}^{-1}$  to  $525\text{ cm}^{-1}$  and from  $1045\text{ cm}^{-1}$  to  $1095\text{ cm}^{-1}$ ; the cause of these displacements could be attributed to the presence of crude palm oil, retained in the pores of the diatomite, which produces interactions with both the support material and the organic phase of the PCM [40].

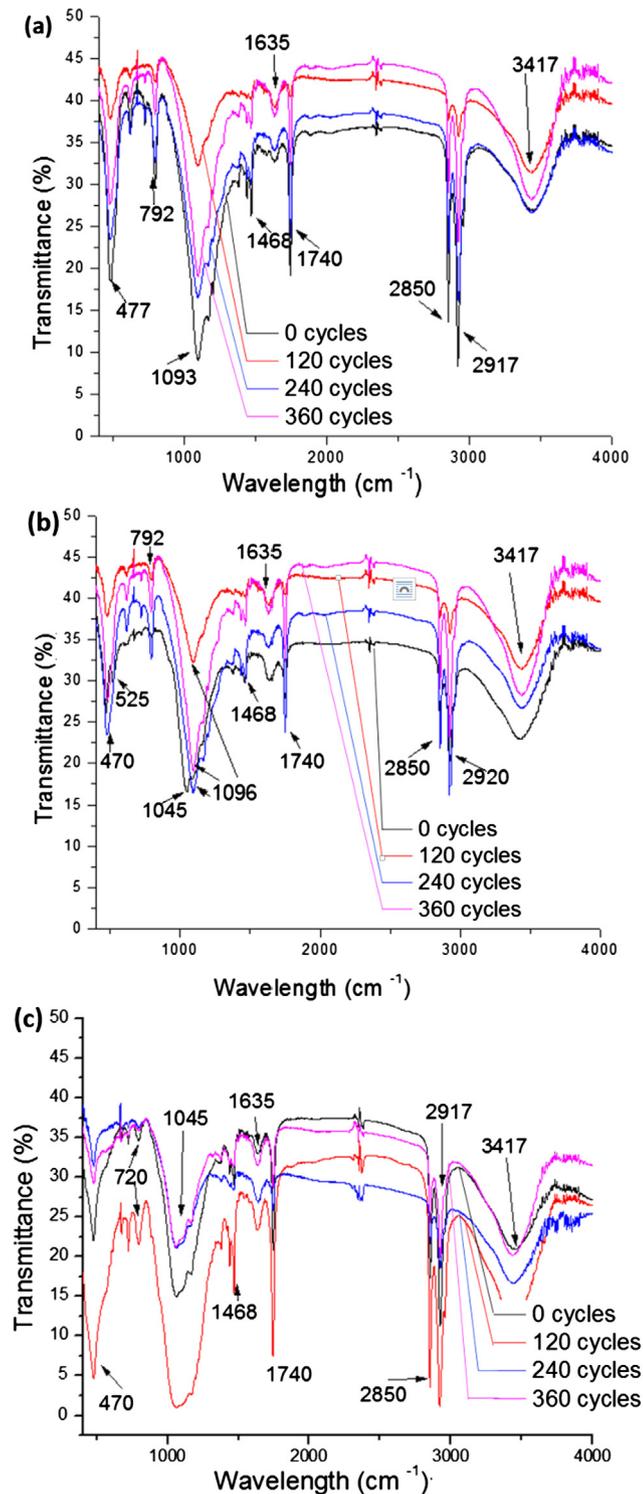


Fig. 7. A) FT-IR spectra of the PCM/new diatomite, B) FT-IR spectra of the PCM/spent diatomite, C) FT-IR spectra of the PCM/calcined diatomite before and after the application of 0, 120, 240 and 360 thermal cycles using 100% commercial stearic acid esters.

Therefore, it was determined that there is no chemical interaction between the support material and the organic phase, by impregnating the esters on the new and calcined diatomite [1].

Additionally, it is observed that both the PCMs constituted by new diatomite and calcined diatomite present chemical stability, since the peaks that present the spectrograms, before and after

the application of the thermal cycles, coincide. The presence of a peak at  $792\text{ cm}^{-1}$  attributed to the O–H group and the displacement of  $1045\text{--}1096\text{ cm}^{-1}$ , which for both cases correspond to the vibration of the Si–O–Si bond [8]. However, these peaks correspond to bonds present in the new and calcined diatomite, so that the chemical stability of the PCMs supported on spent diatomite is not affected by the application of the thermal cycles.

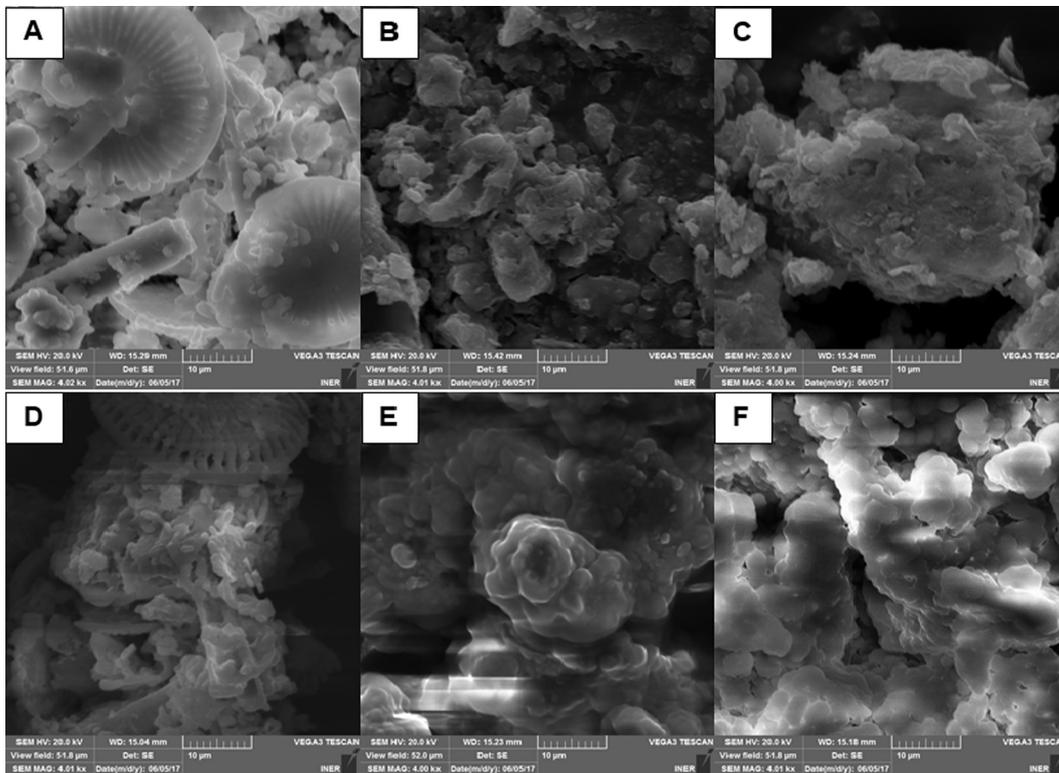
The increase of the latent heat of fusion was greater for both the PCMs supported in new and calcined diatomite after 120 thermal cycles as was shown in Fig. 4. For that reason, the changes in the microstructure of the PCMs were analyzed at that cycle. In Fig. 8D–F, it is evident that the PCMs present an ordering of the esters on the support material after the application of the thermal cycles. During the heating and cooling of the PCMs, the temperature conditions leading to the formation of crystalline zones were precipitated. Because the fatty acid esters are polymers, and most polymers go through a heterogeneous nucleation (crystallization) process when the temperature reaches the melting and solidification points. Then, this rearrangement is produced by the nucleated spherulites formation resulting in an increase in the latent heat of fusion [42,45].

However, for the PCMs impregnated in recycled-calcined diatomite, after the 120 thermal cycles, the degree of the ester molecules ordering is greater, due to the formation of rounded lamellas that are established one on the other. It should be emphasized that the heterogeneous nucleation process is favored when other materials (inorganic components, catalysts and even other polymers) are added to the polymers [42]. Then, to determine the agent that acted on these lands, FT-IR analysis presented in Fig. 6 and SEM analysis presented in Table 4 were used. In the spectrograms, a higher peak area in the calcined diatomite is observed than in the spent diatomite, at  $540\text{ cm}^{-1}$  and  $539\text{ cm}^{-1}$ , respectively, and which is not evident in the new diatomite. According to [44], the bands of the FT-IR of  $500\text{--}670\text{ cm}^{-1}$  correspond to the vibration of the O–P–O bonds. Chemical analysis confirmed the presence of phosphorus in 0.55% in the spent diatomite and in 1.21% in the calcined diatomite, and the new diatomite do not present this element.

Then, as [46] shown, carotenoids and phosphatides are retained in palm oil bleaching earth after their use. Specifically, in the study carried out by [40], it was found that crude palm oil has a phosphorus content of  $(19.1 \pm 0.02\text{ mg/kg})$  and  $(454.0 \pm 5.5\text{ mg/kg})$  of carotenoids remaining in the diatomite during the bleaching process [46,47].

Therefore, it was determined that the agent, which probably facilitates the crystallization of the esters, corresponds to the inorganic part of the phosphatides present in the spent diatomite from the crude palm oil bleaching process. This is verified by the results of the FT-IR analyzes which indicated the presence of O–P–O bonds in both the spent and calcined diatomite. In the calcined diatomite, a higher concentration of these bonds was evidenced than in the diatomite. This can be explained by the fact that, when high temperatures are applied, most organic compounds are volatilized, including carotenoids, resulting in increased concentration of the O–P–O bonds in calcined earth [29].

This study shows that the spent diatomite can be used as support material for PCMs, if it is thermally treated, calcined; since this process facilitates the action of the nucleation and crystallization agents that allow to improve the thermal properties of the PCMs. Specifically, increasing the latent heat of fusion and the resistance to thermal degradation as the heating-cooling cycles pass. Moreover, the drawbacks of the use of spent diatomite without heat treatment, such as the organic phase leakage during the application of thermal cycles and the reduction of its thermal degradation resistance were established.



**Fig. 8.** Summary of scanning electron microscopy results. Microstructure of the PCM supported in (A) new, (B) spent, and (C) calcined, diatomite before the application of thermal cycling at 4000 increases using 100% commercial stearic acid esters. Microstructure of the PCM supported in (D) new, (E) spent, and (F) calcined, diatomite after the application of 120 thermal cycling at 4000 increases using 100% commercial stearic acid esters.

**Table 4**

Chemical analysis of new, used and calcined diatomite.

Element	New diatomite		Used diatomite		Calcined diatomite	
	Percentage (%)	Error (%)	Percentage (%)	Error (%)	Percentage (%)	Error (%)
Carbon	26.99	12.77	43,73	22,39	10,61	7,08
Oxygen	51.49	17.98	41,14	20,00	54,77	18,96
Magnesium	0.03	0.09	1,04	0,32	1,86	0,39
Aluminum	0.57	0.18	2,31	0,46	5,26	0,77
Silicon	19.36	2.11	9,29	1,27	21,22	2,42
Phosphorus	–	–	0,55	0,18	1,21	0,24
Sulfur	–	–	0,22	0,13	0,69	0,17
Potassium	–	–	–	–	0,16	0,11
Calcium	0.59	0.15	0,65	0,17	2,16	0,27
Titanium	–	–	–	–	0,03	0,09
Iron	0.20	0.12	1,05	0,22	1,88	0,24
Copper	–	–	–	–	0,14	0,11
Sodium	0.78	0.27	–	–	–	–

#### 4. Conclusions

In this study recycled-calcined diatomite, residue of the bleaching process of palm oil production, was used as a potential support material for organic and renewably sourced PCMs (commercial stearic acid ester). This material improves the thermal performance of the PCM. the phosphorus contained in the spent diatomite, the nucleating agent (crystallization), allows to increase the latent heat of fusion in 54.80%, and the resistance to thermal degradation, and after 360-cycle thermal test the PCMs presented good chemical compatibility between the support material and the organic phase. The application of thermal cycles determined the long-term thermal and chemical stability of the materials. For that

reason, they can be applied as systems of thermal energy storage in buildings.

Our results show that the use of a recycled material, spent diatomite, provides a comparable chemical and thermal performance with the PCMs supported in new (raw) diatomite. Our work capitalize the advantages of use recycled diatomite such as cheaper materials, better thermal performance during the thermal cycles, less quantity of fulfilled diatomite. These properties make these PCMs effective, environmental friendly, and profitable.

#### 5. Declarations of interest

None.

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