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Regeneration of Waste Diatomite from Palm Oil Production Process as a Support Material for PCMs in Thermal Energy Storage in Buildings

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Abstract. In this study, the use of spent diatomite, an industrial waste in the palm oil production process, was evaluated as a support material for phase change materials (PCMs). Calcination tests of the diatomite were carried out at different temperatures (400, 550 and 700 °C) and times (1 and 2 h). For the PCMs preparation, the organic phase, mixtures of palm oil and commercial stearic acid esters, were impregnated on calcined diatomite under vacuum. Differential scanning calorimetry (DSC) analyses were performed in order to select the PCM with the highest latent heat of fusion and a range of phase change temperature corresponding to the thermal comfort range. DSC, TGA and FT-IR analyses were performed before and after the application of 360 thermal cycles to establish the thermal and chemical reliability of the PCM. It was found that 700 °C and 1 h are the best conditions of the calcination process, and the PCM consisting in 100 % methyl esters of commercial stearic acid presented the highest value of latent heat of fusion (34.67 J/g) and a phase change temperature range of 16,4 to 33,5 °C. After the thermal cycles, the results show that the prepared PCMs has thermal and chemical stability.

Introduction

The energy required for the operation of air conditioning systems, is mainly sourced from fossil fuels [1]. However, the use of fossil fuels for energy purposes represents a constant environmental concern, since its use is associated with greenhouse gases emissions [2]. The use of renewable energy sources, such as thermal energy storage systems and PCMs, can reduce the energy consumption associated to the use of air conditioning systems in buildings [3].

The use of PCMs in buildings requires materials that present phase change temperature ranges that correspond to the thermal comfort range (18-30 °C), and with high values of fusion heat [4]. In such conditions, a PCM improves the level of thermal comfort and reduces temperature fluctuations in buildings [2]. Also, chemical and thermal stability of PCMs should be evaluated with the application of thermal cycles, which can generate changes in both the chemical structure and thermal properties (latent heat of fusion and temperature range of phase change) of the material exposed to these cycles [1].

Fatty acid esters have good chemical stability, are non-toxic, non-corrosive, and renewably-sourced; furthermore, in their liquid state they have sufficient surface tension to be retained in porous support materials [5]. Specifically, Xu et al. (2014) ascertained that methyl stearate and methyl palmitate mixtures have a great potential as PCMs for buildings and can be sourced renewably from palm oil. In addition, PCMs supported on porous materials remain solid even when the melting point is reached at the phase change [6,7].

Diatomite is a porous material with a variety of unique properties such as high porosity, thermostability, excellent absorption capacity, and is chemically inert that enable its use as a support material for PCMs [6]. Currently, diatomite is mainly used in the bleaching process of edible oils [8,9]. However, it is used only once during vegetable oil bleaching, and then it is usually landfilled.

Its final disposition implies both an economic cost and a potential source of soil pollution [9]. Among the different alternatives to the final disposition of spent diatomite, its use as a support material for PCMs needs to be considered. For this reason, the present study aims to provide initial information on the development of phase change materials (PCMs) from residues from the palm oil extraction industry, which currently have no economic value, in order to develop organic PCMs.

Methodology

Calcination test

Different calcination temperatures (400, 550 and 700 ºC) and times (1 and 2 h) of the spent diatomaceous earth were evaluated in order to determine the conditions that allow a better impregnation percentage [8,9]. For this purpose, the calcination tests were performed in an electric furnace by triplicate (n=3). The response variable was calculated by Equation (1), and it corresponded to the percentage of impregnation of palm oil esters in calcined diatomaceous earth at different temperature and time conditions [6]:

$$\% \text{ Impregnation} = m1/(m2 + m3) \times 100 \quad (1)$$

Where:
m1: Total impregnated mass of the organic phase on the support material (g)
m2: Mass of the ester mixture used (g)
m3: Mass of the support material used (g)

The results of the impregnation percentage were statistically analysed using the Statgraphics Centurion XVI software to find the best calcination time and temperature conditions for the studied ranges. These calcination conditions were applied for preparing the thermally treated diatomite used as a support for PCMs.

Preparation of the PCMs

For the PCM preparation, the organic phase, palm oil esters and commercial stearic acid esters mixtures, was impregnated under vacuum pressure on the support material (calcined diatomite).

The support materials were dried at 105 °C for 24 h prior to use [5]. In addition, the procedure described by Xu et al. (2014) for the preparation of the mixtures of palm oil (PO) esters and commercial stearic acid (CSA) esters in 5 different proportions (100 - 0, 75 - 25, 50 - 50, 25 - 75, 0 - 100%) (w/w), was followed [10]. In order to obtain the PCMs, the vacuum impregnation method was applied using a pressure of 27 kPa for 30 minutes [5].

Thermal characterization

In order to determine the PCM that has the most suitable thermal properties to store thermal energy in buildings DSC analyses in a Q 2000 1714, TA Instruments apparatus were done. Measurements were carried out at 0 to 60 °C with a heating rate of 4 °C/min under an inert atmosphere of nitrogen with a flow rate of 20 mL/min [10]. The phase change temperature range considered was from T onset to T end determined by the equipment.

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 thermal comfort was selected [4]. After that, its thermal and chemical stability was evaluated by applying heating and cooling cycles.

Thermal cycles test

To determine the reliability of the PCM, its thermal and chemical stability was evaluated before and after its exposure to the heating and cooling cycles (120, 240 and 360 cycles) [10].

In order to analyze the thermal stability of the PCM, DSC analyses were performed under the same conditions detailed in the last section, and thermogravimetry analyses in a Shimatzu equipment in a temperature range of 25 to 600 °C, with a heating rate of 10 °C/min and a nitrogen flow of 50 mL/min were carried out [5]. On the other hand, an infrared spectrophotometer Perkin

Elmer, Frontier with Fourier transform was used to determine the chemical stability in a wavelength range of 4000 - 400 cm^{-1}. The spectra of the PCM without exposure and exposure to different cycles were compared in order to identify chemical changes in the material produced by the effect of thermal degradation [5].

Results and Discussion

Calcination test

Figure 1 shows that the best conditions for the spent diatomite thermal treatment, within the studied ranges, correspond to 700 °C and 1 h. These results could be explained because of thermal regeneration treatments were carried out without a preliminary extraction process of organic compounds with solvents, so a temperature above 600 °C is required to remove the organic components retained in the diatomite [9]. Exposure of the spent diatomite to temperatures above 500 °C for prolonged periods could cause pore sintering, and therefore the absorption capacity will decrease [9]. The selected conditions allowed a better use of the regenerated earth as support material, since its pores could be occupied by the esters instead of the eliminated organic compounds [8].

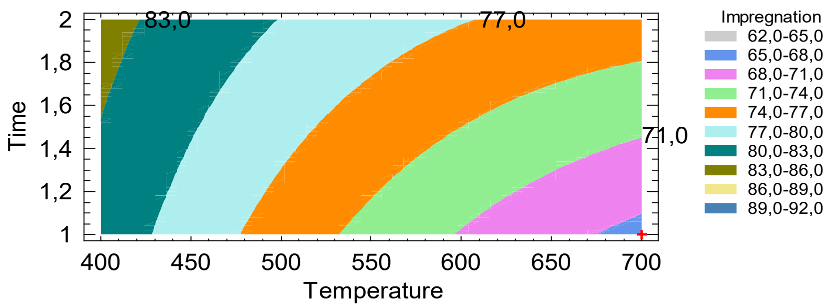

Figure 1. Contour plot for percent impregnation.

Thermal characterization

Table 1 shows the results of the DSC analyses. The latent heat of fusion is higher when 100 % of CSA methyl esters are impregnated in calcined diatomite, and the phase change temperature range is close to the thermal comfort (18 - 30) °C [4]. In addition, it is noted that the phase change temperature range decreases when the content of CSA esters increases, this behavior could be explained since in the ester mixtures while increasing the proportion of CSA esters the content of methyl palmitate and methyl stearate is higher than the other esters, and their phase change temperatures are 31 °C and 39 °C, respectively [10].

Table 2. Temperature range of phase change and latent heat of fusion of the PCMs supported in thermally treated diatomite

Composition of PO esters - CSA esters [%-%]	T onset [°C]	T end [°C]	Latent heat of fusion [J/g]
100-0	0.3 ± 0.1	36.2 ± 2.1	13.71 ± 0.21
75-25	12.3 ± 0.7	26.3 ± 0.9	23.21 ± 2.88
50-50	2.2 ± 0.3	21.3 ± 0.3	21.26 ± 0.35
25-75	2.2 ± 0.4	16.9 ± 2.4	14.01 ± 0.46
0-100	16.4 ± 0.4	33.5 ± 0.6	34.67 ± 2.56

Thermal reliability of the PCM

To determine the applicability of the selected PCM as thermal energy storage system, thermal stability was analysed by DSC and TGA analyses and the chemical stability by FT-IR analyses [10].

The DSC melting curves of the PCM is presented in Figure 2. After 120 thermal cycles, an increase in the curve area representing the magnitude of the latent heat of fusion is evidenced [5]. This increase could allow the material to absorb a greater amount of energy in a smaller mass of the same, facilitating the establishment of thermal comfort conditions in buildings [10].

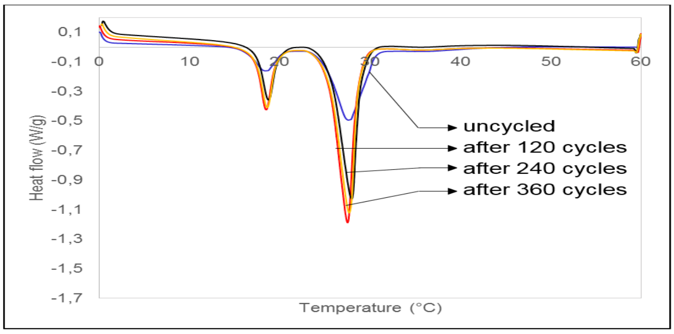

Figure 2. DSC melting curves of PCM supported in calcined diatomite before and after the application of 0, 120, 240 and 360 thermal cycles using 100% commercial stearic acid esters

On the other hand, by the thermogravimetric analyses, it was determined that the PCM do not present degradation at low temperatures as can be seen in Figure 3; since the loss of mass at 100 °C, is less than 2 %. This weight loss could be due to the loss of moisture present in the PCMs [5]. By the TGA analysis it was evidenced that the organic phase does not released of the porous material; since at 100 °C which is a temperature higher than the phase change temperature of the PCM there is no loss of the organic phase [5]. This indicates that the analysed PCMs are thermally stable and can be used as energy storage systems [10].

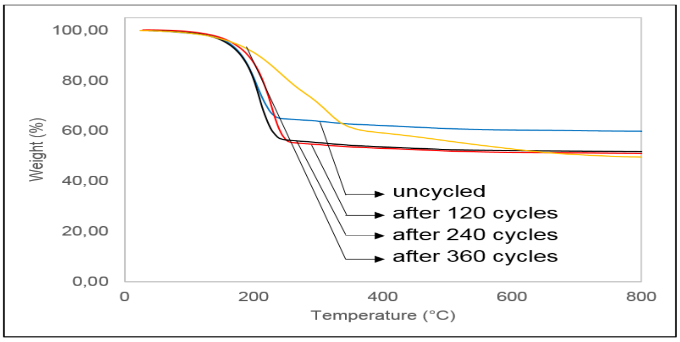

Figure 3. Thermogram of the PCM supported in calcined diatomite before and after the application of 0, 120, 240 and 360 thermal cycles, using 100% commercial stearic acid esters

The FT-IR analyses were performed before and after the application of the thermal cycles in order to identify changes in the chemical structure of the PCM. In Figure 4, it is observed that the peaks of calcined diatomite and the ester are maintained after the impregnation process. Additionally, it is observed that the PCM constituted by calcined diatomite present chemical stability, since the peaks, before and after the application of the thermal cycles, coincide [5].

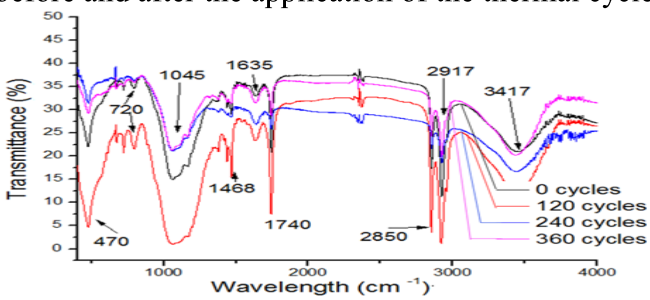

Figure 4. FT-IR spectra of the PCM supported in calcined diatomite before and after the application of 0, 120, 240 and 360 thermal cycles using 100% commercial stearic acid esters

Based on the results obtained, it was found that the calcined diatomite could be used as support material for PCMs; since the PCM does not present a notable change after the application of the thermal cycles. Even though the latent heat of fusion increased in almost double in PCMs supported in calcined diatomite, from 30.12 to 53.67 J/g, the FT-IR analyses do not show changes in the chemical structure, and TGA analyses show that the selected PCM works well in the range of comfort temperature.

Conclusions

With methyl esters, thermally treated diatomite can be used as a recycled support material for renewable and non-toxic PCMs in order to maintain comfort temperatures in buildings.

PCM with 100 % of methyl commercial stearic acid esters reached a latent heat of fusion 34.67 J/g and a phase change temperature range of (16.4 – 33.5) °C.

PCM supported in calcined diatomite presented thermal and chemical reliability, so it can be used in thermal energy storage in buildings.

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