Energy 278 (2023) 127692

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

New hybrid bio-composite based on epoxidized linseed oil and wood particles hosting ethyl palmitate for energy storage in buildings

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ARTICLE INFO

Handling Editor: Dr X Zhao

Keywords:
Bio-based PCMs
Bio-composite
Building applications
Energy storage
Epoxidized linseed oil
Ethyl palmitate
Wood particles

ABSTRACT

In this study, the incorporation of ethyl palmitate (EP) as a bio-based phase change material (BPCM) in wood particles, the preparation and properties of the novel biocomposite for building applications were investigated. The wood particle-based composites hosting BPCM were produced by cold compression moulding. The EP impregnation step was optimized in terms of uptake and its ratio by post-addition of non-impregnated fibers. The optimized wood particles/EP ratio were combined with 37.5% epoxidized linseed oil (ELO) as a binder to produce a composite with energy storage function containing more than 99% bio-ingredients. The optimum BPCM content in the composite was 25%. The produced biocomposites were characterized by T-hystory, DSC, TGA, and a moisture buffer test. The results revealed excellent moisture buffer values (2.07 g/m^2 RH%) according to the Nordtest protocol, significant thermal mass, ability to store excessive energy in terms of latent heat and maintain the temperature constant for longer time, good thermal stability and improved specific heat capacity when compared to a reference composite without BPCM. The effect of incorporating BPCM into biocomposite for regulating temperature fluctuations was confirmed by comparing test prototype cubes, with and without BPCM, subjected to temperature fluctuation between 0 and 40 °C.

Author contributions

The conceptualization, methodology, writing and editing were through equal contributions of all authors who have given approval to the final version of the manuscript. All authors have read and agreed to the published version of the manuscript.

1. Introduction

The present energy and environmental issues are bringing new areas of research related to sustainable and renewable materials in construction industry. Being used for centuries, wood and wood-based composites are the main source of renewable materials in building applications [1–3]. Due to the intrinsic properties of wood, e.g. high strength-to-weight ratios, thermal and acoustic insulating properties, availability, low price and relatively lightweight, this material has been of interest in construction industry [3].

Nowadays, engineered wood products of new timber systems, e.g. konstruktionsvollholz (KVH), duo/trio laminated beams, cross-laminated timber (CLT) and laminated veneer lumber (LVL) are extensively used in construction applications [4]. In addition, by-products generated in sawmills such as wood flour, chips, particles, sawdust, and fibers are used in production of high value wood panels not only adding value to the originally less valuable by-product but also reducing and managing wastes. Moreover, the porous nature of these by-products, in particular wood fibers and sawdust, can be used to encapsulate BPCMs to produce energy smart wood-based panels for passive energy storage in buildings [5–9].

In this regard, solid wood impregnated with BPCM has been the topic of a number of studies considering different wood species and thermally treated wood. The studies [10,11] showed that solid wood impregnated with BPCM has higher thermal mass compared to non-impregnated wood and can serve as energy smart material for building applications. The studies revealed that leakage of the BPCM is a serious obstacle regarding incorporation of BPCMs in solid wood. Recently some attempts have been undertaken to combine fruit shells and BPCM as energy smart composites for building applications. Hekimoğlu et al. [8,12,13] in a series of studies investigated the possibility of using walnut, apricot and hazelnut shells impregnated with BPCMs for producing energy smart panels. The porous structure of the ground fruit shells

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https://doi.org/10.1016/j.energy.2023.127692
Received 29 September 2022; Received in revised form 4 April 2023; Accepted 28 April 2023

allows these materials to be impregnated with PCMs and combined in composites that are chemically and thermally stable with less or no leakage during testing. Other studies [14,15] investigated incorporation of a BPCM in wood fibers and waste sugar beet pulp. It was reported that the products were thermally and chemically stable within appropriate working temperature and enthalpy with no leakage.

Wood flour and veneers have been studied as cheap bio-containers for encapsulation of PCMs for building application [2] where the produced composites with BPCMs are incorporated in the internal walls, floorings [16], and coatings [17] or in the façades of the buildings [18]. A number of studies used wood flour [6,7,19–21], modified solid wood and wood composites [22–24] as bio-container for hosting PCMs making energy smart bio-composites for building applications. In some of the studies, fossil-based binders, e.g. thermoset plastics [21,25], have been employed, while others only moulded the fibers impregnated with BPCMs without using reasonable press load or even binder, i.e. these materials can hardly be classified as stable bio-composites.

Some fatty acid esters offer working temperature ranges appropriate for passive energy storage in building application. Ethyl palmitate (EP) was reported as a promising BPCM with thermal properties suitable for building application [26]; however, to our knowledge, EP has not been yet studied in combination with wood materials as a container. Moreover, most of the studies regarding bio-composites made of wood fibers or particles have not used pressing, which is an inevitable step during the production of bio-based composites.

In the present study, ethyl palmitate (EP) was used as BPCM and its incorporation in wood particles was comprehensively investigated. The thermal properties of the novel wood particles reinforced composites hosting BPCM were studied and compared to the controls without BPCM.

2. Experimental

2.1. Materials

Ethyl palmitate (EP) was purchased from Sigma-Aldrich. Pine wood sawdust (*Pinus sylvestris* L.) was provided from Sätra sawmill near Uppsala, Sweden. Spruce mechanical pulp fibers was provided from Stora Enso. Epoxidized linseed oil (ELO) was purchased from Traditem GmbH, Germany.

2.2. Methods

2.2.1. Incorporation of EP into wood particles and fibers

EP ester was impregnated into wood particles by a vacuum-pressure process in an autoclave. Before impregnation, the sawdust particles were dried at 80 °C for 24 h and sieved to obtain a fraction of ~2 mm. The autoclave temperature was set at 60 °C to ensure melting of EP, then the wood particles were immersed in the ester and a vacuum of 350 mbar was applied for 10 min followed by 6 bar pressure for 1 h. The achieved weight percentage gain (WPG%) was calculated according to Eq. (1) [10,11].

$$\mathrm{WPG\%} = \frac{(m_f - m_i)}{m_i} \times 100 \tag{1}$$

where m_i and m_f are the initial and final mass of the samples.

After the impregnation, the wood particles was placed in a funnel in an oven set at 40 °C for 24 h to leach the redundant EP. This was done to minimize the amount of ester at the surfaces of the impregnated materials. The leached particles were then put on tissues to absorb the residual EP on particles' surfaces.

2.2.2. Composite elaboration

In order to minimize the leaching of BPCM and increase the adhesion between the wood particles substrate and the polymeric matrix, a portion of non-impregnated mechanical pulp fibers was added to the impregnated wood particles prior to mixing with the polymeric matrix. The non-impregnated fibers were sieved to a fraction of ~2 mm. The amount of impregnated wood particles in the composite was 50% (25% wood particles and 25% EP), while the non-impregnated fibers represent 12.5% of the total weight of the composite. Epoxidized linseed oil (ELO) (37.5% in the composite) was used as a binder in the composite. ELO was pre-polymerized by adding and mixing 0.2% of a strong Lewis acid at room temperature, and then mechanically blended with impregnated wood particles and non-impregnated fibers.

After mechanical mixing of the ELO-binder with the fibers, the blend was transferred into a Teflon mould and cold pressed at room temperature at 12.3 kg/cm^2 pressure for 45 min. After pressing, the mould were placed in an oven set at 50 °C for 12 h for polymerization. Fig. 1 shows graphically the production process of wood particles/fibers reinforced composites. It should be mentioned that for control samples (composites without BPCM), identical processing was employed with non-impregnated materials. The dimensions of the produced composite samples were 9 × 90 × 90 mm.

2.2.3. Hygroscopicity measurements

Hygroscopicity of the prepared composites with and without BPCM was conducted, using samples with dimension of 9 × 90 × 90 mm, in a climate chamber according to the Nordtest Project protocol [27], following the same schedule as reported in Ref. [15], with some modifications. Moisture buffer value (MBV), which is the amount of moisture that a material can store and release during the relative humidity oscillations of the environment [15] was measured. The test was carried out at constant temperature of 23 °C. The samples were first preconditioned at 50% RH for 24 h, weighed and then placed back in the climate chamber at RH 75% for 24 h. After weighing the samples, the RH was increased to 95% and then RH decreased to 33%, while the mass of the samples was measured at an interval of 24 h. MBV was calculated as follows [15,27]:

$$\mathrm{MBV} = \frac{\Delta m}{A(RH\%_{max} - RH\%_{min})} \times 100 \tag{2}$$

where Δm is the mass variation during the absorption/desorption phase, A is the sample surface area and RH_{max}, RH_{min} is the maximum and minimum relative humidity.

2.2.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) thermograms of the BPCM and wood particles composites containing BPCM were recorded on a DSC Mettler-Toledo DSC 3 system under a nitrogen atmosphere. For each DSC run, a sample of mass usually in the range 20–30 mg was taken from the core of the composite sample and in liquid phase for the ethyl palmitate (BPCM) and hermetically sealed in standard DSC aluminum crucible pan. As discussed in Ref. [28] a lower cooling rate can give a better result therefore the DSC tests were conducted between 0 and 40 °C at a heating rate of 2 °C/min and cooling rate of 1 °C/min with 5 min isothermal segment at each 0 °C and 40 °C. This heating-cooling cycle was repeated three times to obtain an acceptable reproducibility. Prior to measurements, the DSC system was calibrated using indium and zinc.

2.2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) thermograms of the BPCM, epoxidized linseed oil polymer and wood-ELO composite containing BPCM were recorded on a TGA Mettler-Toledo TGA 2 system under a nitrogen atmosphere. For each TGA run, a sample of mass usually in the range 20–30 mg was taken from each sample and placed in a standard alumina (aluminum oxide) crucible pan. The TGA tests were conducted between 26 °C and 500 °C at a heating rate of 10 °C/min with 5 min isothermal segment at 26 °C and 500 °C.

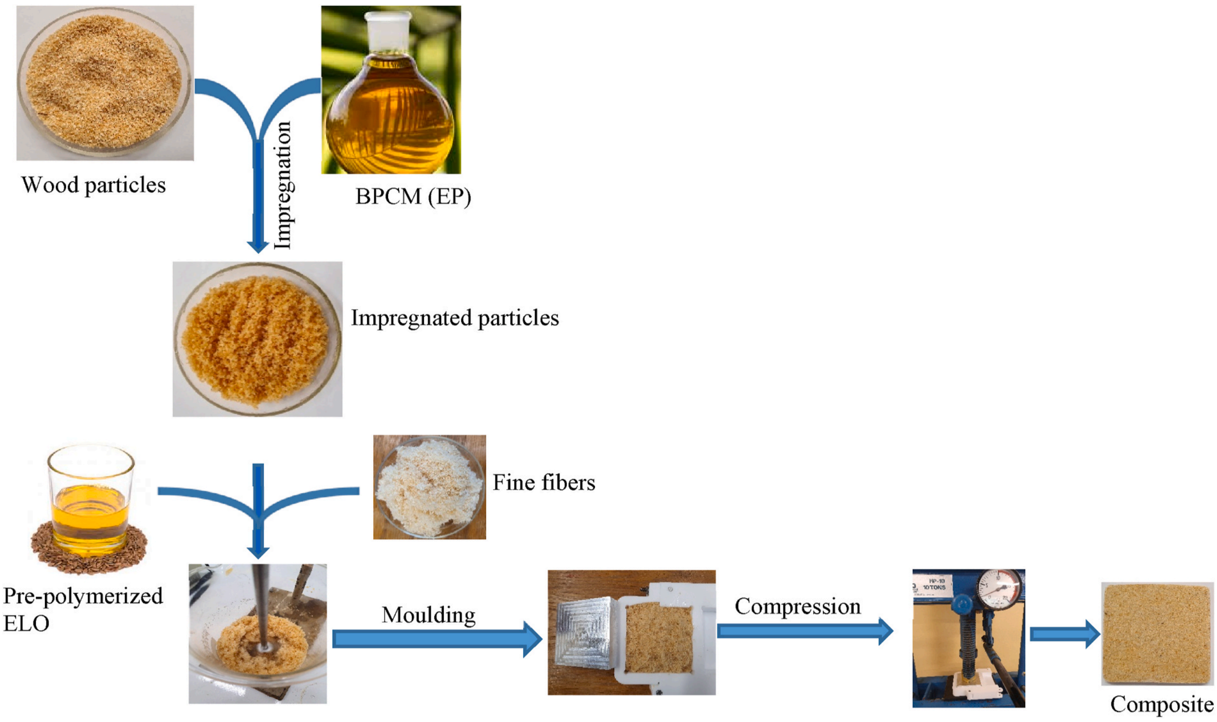

Fig. 1. The process of producing wood particle composite with BPCM.

2.2.6. T-history, specific heat capacity and enthalpy

T-history method was used to measure thermal properties of several samples simultaneously [29,30] including melting/freezing point, latent heat of fusion, degree of supercooling and specific heat capacity. In order to measure thermal properties of pure EP (BPCM), the same T-history set up used in Ref. [28] was employed. BPCM sample and ultrapure water as reference were tested simultaneously. Stainless steel tubes (SS316) with internal diameter of 10 mm, 1 mm wall thickness and 150 mm length were used as containers for BPCM sample and reference. The containers were filled up to 140 mm, while 10 mm was left for possible volume expansion during heating/cooling cycles. The containers are thermally insulated using 10 mm thickness ARMAFLEX insulation material. K-type thermocouples were used to record temperature changes over time for each sample and reference. The thermocouples were placed at the centerline and in the middle of each container. For cold and hot ambient, two separate chambers were employed, a climate chamber was used as cold ambient fixed at 0 °C, and an oven was used as hot ambient fixed at 35 °C, the ambient chamber/oven temperatures were recorded with two separate thermocouples. Sample and reference were first preheated in the oven at 35 °C, and then quickly transferred into the climate chamber at 0 °C and the temperature profile was recorded. Once the equilibrium temperature was reached (ca. 3 h), the sample and the reference tubes were transferred into the oven at 35 °C and the temperature changes were recorded.

For thermal properties of the composites, the same T-history method reported in Ref. [10] was employed. Samples of ELO/particles composite with and without BPCM with dimension of 9 × 90 × 90 mm, and a copper (Cu) plate as reference with identical dimensions were tested simultaneously (Fig. 2). The samples and reference were thermally insulated using 10 mm thickness ARMAFLEX insulation material. K-type thermocouples were used to record temperature changes over time for samples and the reference. The thermocouples were placed at the centerline and in the middle of the samples. For cold and hot ambient climates, two chambers were employed, the former used for cold

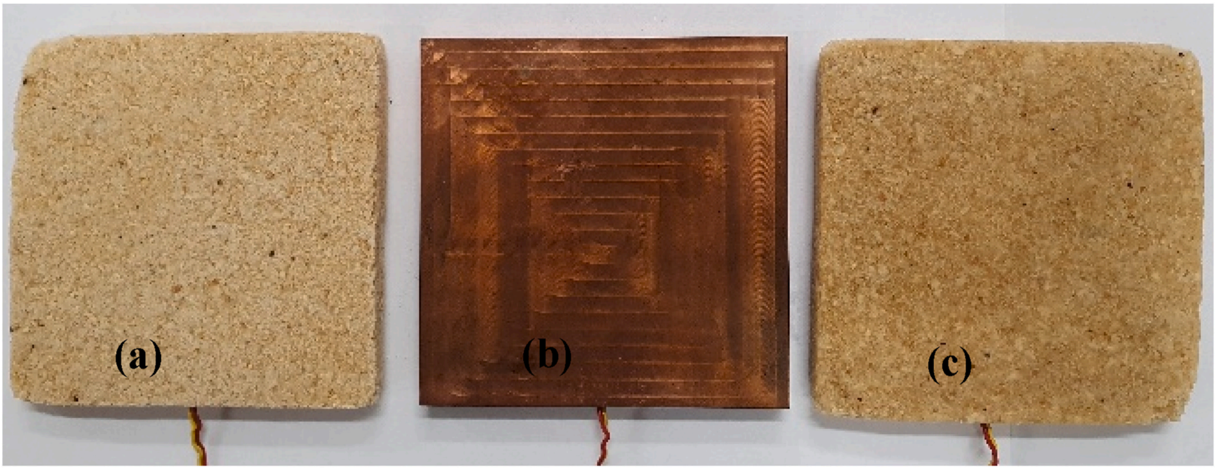

Fig. 2. The samples and reference for T-history test without insulating material; (a) composite without BPCM, (b) Cu and (c) composite with BPCM.

ambient climate fixed at 0 °C, while the latter chamber was used for hot ambient climate set at 40 °C. The chamber's temperatures were recorded with two separate thermocouples. Samples and the reference were first preheated at 40 °C, and then quickly transferred into the chamber at 0 °C and the temperature profile was recorded. Once the equilibrium temperature was reached (ca. 3 h), the samples and the references were transferred back at 40 °C and the temperature changes were recorded.

Energy balance for the reference was employed to obtain the overall heat transfer coefficient [10,11]. Since the samples and the reference have identical dimensions and insulation for uniform heat transfer conditions, the overall heat transfer coefficient (u) for both reference and samples were considered identical. The amount of heat transferred to/from samples in the chamber is expressed as follow:

$$Q = uA\left(T(t)_n - T_\infty\right) \tag{3}$$

where Q, u, A, $T(t)_n$ and T_∞ are respectively the transferred heat, overall heat transfer coefficient, heat transfer area, sample temperature at each time point and ambient temperature inside oven/chamber.

The amount of heat stored/released in/from samples is:

$$Q = mC_p \frac{d\left(T_i - T(t)_n\right)}{dt} \tag{4}$$

where m, C_p, T_i and dt are respectively the mass of the samples, specific heat capacity, initial temperature and time interval.

The amount of transferred energy to/from the samples is stored/released in/from the samples, then the energy balance is:

$$Q = -uA\left(T(t)_n - T_\infty\right) = mC_p \frac{d\left(T(t)_n - T_i\right)}{dt} \tag{5}$$

By rearrangement and integration, the temperature distribution for the reference and samples are obtained as:

$$\int_{T_i}^{T_n} \frac{d\left(T(t)_n - T_\infty\right)}{\left(T(t)_n - T_\infty\right)} = -\int_0^{t_n} \frac{uA}{mC_p} dt \tag{6}$$

After mathematical operation:

$$\ln\left[\frac{\left(T(t)_n - T_\infty\right)}{\left(T_i - T_\infty\right)}\right] = -\frac{uA}{mC_p} t_n \tag{7}$$

As the thermo-physical properties of the references is known, the overall heat transfer coefficient (u) is calculated using energy balance for the reference:

$$uA = -\frac{\ln\left[\frac{\left(T(t)_n - T_\infty\right)}{\left(T_i - T_\infty\right)}\right]_{ref}}{t_n} m_{ref} C_{p,ref} \tag{8}$$

uA is calculated by the energy balance for the reference according to Eq. 8, and as heat transfer area and conditions around reference and samples are identical, uA was calculated from the energy balance of the reference and used further to calculate C_p for the samples. After substitution Eq. (8) in Eq. (7), C_p of the samples is calculated as:

$$C_{p,samp} = \frac{\ln\left[\frac{\left(T(t)_n - T_\infty\right)}{\left(T_i - T_\infty\right)}\right]_{ref}}{\ln\left[\frac{\left(T(t)_n - T_\infty\right)}{\left(T_i - T_\infty\right)}\right]_{samp}} \frac{m_{ref}}{m_{samp}} C_{p,ref} \tag{9}$$

Enthalpy of the samples is obtained as:

$$\Delta H = c_{p,samp}\left(T(t)_{n,samp} - T_{samp,i}\right) \tag{10}$$

where ΔH is enthalpy change from initial point to each time point n.

2.2.7. Effect of BPCM on thermal properties of composites - small model cubes

Two identical cubes with a side length of 90 mm were designed to test the thermal cycling stability and effect of incorporation of BPCM into wood particles-ELO composites. Samples (9 × 90 × 90 mm) with and without BPCM were produced and assembled into two cubes. The cubes were insulated with 10 mm thickness ARMAFLEX insulation material. Two thermocouples were placed inside each cube set at the middle of the cubes to record the temperature profile over time (Fig. 3). The cubes were placed in a climate chamber with a scheduled temperature program oscillating between 0 and 40 °C. First, the climate chamber temperature was set at 20 °C for 30 min, then the temperature increased to 40 °C with heating rate of 1 °C/min followed by 3 h isotherm at 40 °C, and then decreased to 0 °C with cooling rate of 1 °C/min followed by 3 h isotherm at 0 °C. The heating/cooling process was repeated 10 times followed by 2 h rest time and 10 more cycles were carried out. The temperature changes in the cubes and the climate chamber environment were monitored.

3. Results and discussions

3.1. Impregnation and leaching tests

One of the main challenges with incorporation of PCM in fibers/particles composites is the intensive leaching of the PCM during the compression-moulding step. In order to optimize the composite elaboration with acceptable mechanical performance and less leaching, several strategies were tested by varying the proportion of non-impregnated fibers fraction in the composites, as well as varying the load exerted on the composites during compressing moulding. In this study, the wood particles were used as capsules for BPCM, while the non-impregnated fiber fraction was used as a filler to absorb extra ester from the surfaces of the particles, thus favoring the polymerization of ELO. These fibers have also a function to absorb the squeezed ester during the pressing step and retain the BPCM during the exploitation. The advantage with using sawdust particles is that this material is cheap with almost no industrial application and normally used for burning. Therefore, when these materials are used as bio-container to host BPCM producing energy smart panels for building applications, this can add value to less valuable by-products and management of wastes as well. Results showed that, the optimum proportion of impregnated particles in the composites was 50% (25% particle, 25% EP) while the proportion of non-impregnated fibers was 12.5% of the total mass of the composite, and ELO was 37.5%. Experiments showed also that the optimum load ensuring acceptable mechanical properties with reasonable PCM uptake was 1 ton (12.3 kg/cm^2 pressure). The curing/polymerization of ELO was performed at 50 °C for 12 h, and no mass loss (leaching) was noticed during the process as well as during the conditioning at room temperature. Depending on the applied load, part of the BPCM can be pressed out during the stage of moulding. When loads less than 12.3 kg/cm^2 were exerted on the composite, no PCM was pressed out, but after curing, the residual/excessive PCM present on the particles' surfaces was gradually migrating to the surface of the composites forming crystal on the surfaces, when the produced composites were stored at room temperature. This phenomenon was not observed for composites produced with loads of 12.3 kg/cm^2 and larger as most of the residual PCM was pressed out during the pressing step. Probably, the excessive PCM around and between fibers/particles is either removed during pressing when high loads were applied, or migrates to the composite surface and forms crystals when insufficient load is applied. The later phenomenon could be considered as leaching although it does not occur during the polymerization step at 50 °C. The above observations have not been discussed in the literature as most of the produced composites were either small, or no loads were applied during the composites elaboration [12–14]. Fig. 4 shows the final optimized products of sawdust composite with BPCM.

3.2. Moisture adsorption and MBV of the composites

Fig. 5 shows moisture adsorption values of the composites with and

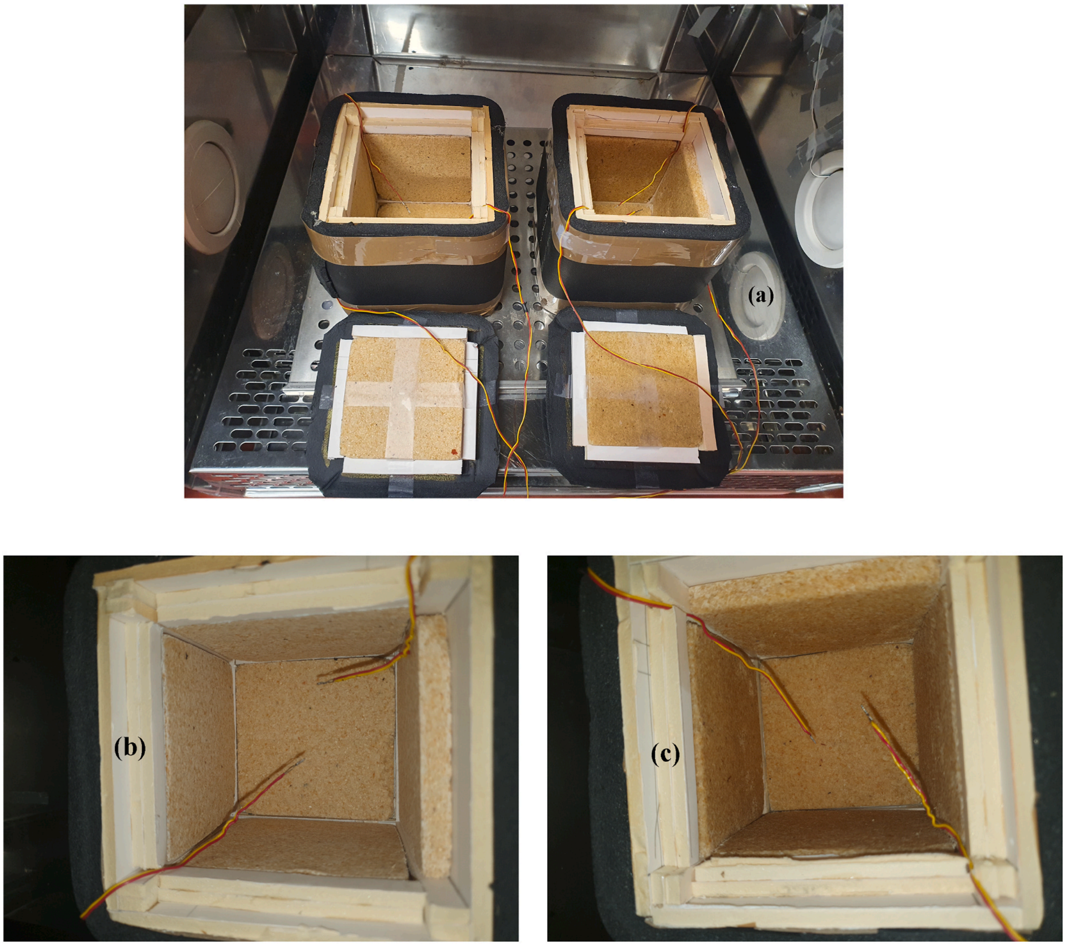

Fig. 3. Experimental set of cubes for cycling test; (a) cubes with the lids in the climate chamber, (b) cube for composite without BPCM and the position of thermocouples, (c) cube for composite with BPCM and the position of thermocouples.

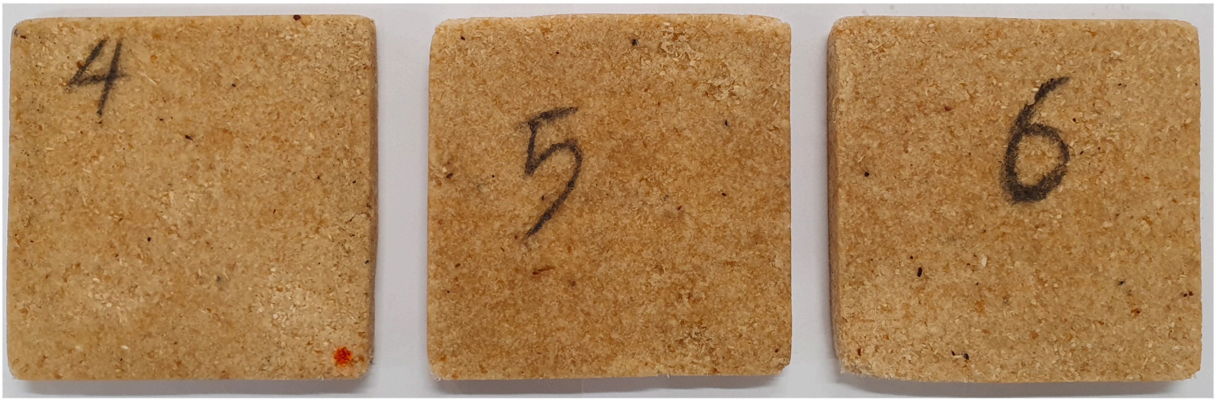

Fig. 4. Samples of optimized wood particles composite with BPCM.

without BPCM. The increase in the relative humidity provokes higher moisture adsorption in the composites. It was expected that the weight of the samples at 50% RH will be higher than the initial weight but it was observed that at 50% RH, the samples lost some moisture, i.e. they dried. When the sample weights at 50 and 95% RH are compared, an increase in the weight with 3.6% for the composites with BPCM and 5.9% for the composite without BPCM was observed, i.e. the BPCM in the composite reduces the moisture adsorption. When the sample weights at maximum (95%) and minimum relative humidity (33%) are compared, the ability of the material to regulate the moisture within its moisture capacity, i.e the MBV [15,27] was calculated. The composite with BPCM lost 3.3% of its weight while the composite without BPCM lost 6.8%; the calculated MBV for the composite with BPCM was 2.07 g/m^2 RH%, and for the composite without BPCM was 3.2 g/m^2 RH%. The MBV for both composites is higher than 2 g/m^2 RH%, which is in the range of excellent category according to Nordtest protocol [27]. The lower MBV for the composite with BPCM than that without BPCM is caused by the impregnated BPCM into the wood structure that hinders and slows down the adsorption rate leading to lower ability of the material to regulate moisture. However, the MBV still categorized the material as excellent

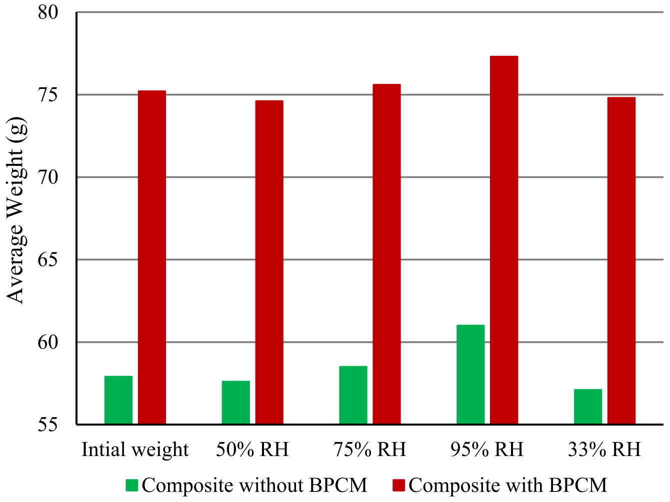

Fig. 5. The moisture adsorption test of the samples (n = 3 samples for each type of composites) at various relative humidities according to the Nordtest protocol.

humidity regulator according to the protocol.

3.3. *Thermal stability of the composite*

The Thermal stability behaviors of pure EP, ELO polymer and composite hosting BPCM were conducted using TGA under nitrogen atmosphere. Fig. 6 shows that ELO polymer curve has a sigmoidal shape, indicating a single mechanism of degradation, with almost no weight loss below 325 °C indicating a good thermal stability. Above 325 °C, the polymer starts to degrade until complete degradation around 475 °C. The thermal degradation pattern for EP comprises two steps; the first starts at 150 °C and up to 220 °C, in which the material losses ca. 24 wt %, due to decomposition of ester moieties, then the decomposition proceeds until 325 °C, leaving no residue. The degradation pattern for the composite hosting BPCM occurs in three stages. The small mass loss below 100 °C, is mainly due to the evaporation of residual moisture and other solvents used during composite manufacturing. The first stage stars at around 100 °C and up to 210 °C, the material loses 4 wt%. The second step is mainly related to the degradation of the EP starting at temperature around 210 and up to 320 °C where almost all EP is degraded and the composite shows a loss of 33 wt%. The last stage is related to degradation of the used polymer, sawdust and fibers forming the composites, and starts at ca. 325 °C and up to 450 °C, leaving 10% residue. The result shows that the materials, in particular the composite is thermally stable within the expected working temperature range and degradation for this material starts at a temperature of ca. 200 °C.

3.4. *Thermal analysis by DSC, T-history and thermal cycling in small cubes*

Fig. 7 shows the DSC curves obtained for EP (BPCM), and the composite with BPCM. For pure EP, during the course of cooling two peaks are observed showing incongruent freezing at two different temperature peak points at 17 °C and 15 °C. During the course of heating, although only one main peak is observed, the material shows certain changes at the peak related to probably polymorphic nature of the material [31, 32]. The pure EP starts to melt (onset temperature) at 23 °C and fully melted at 30 °C (endset temperature). The general pattern of the curve for the composite with BPCM is almost similar to pure EP but those changes at melting peak point related to polymorphism is not observed and some degrees of shift in onset and endset temperatures can be seen.

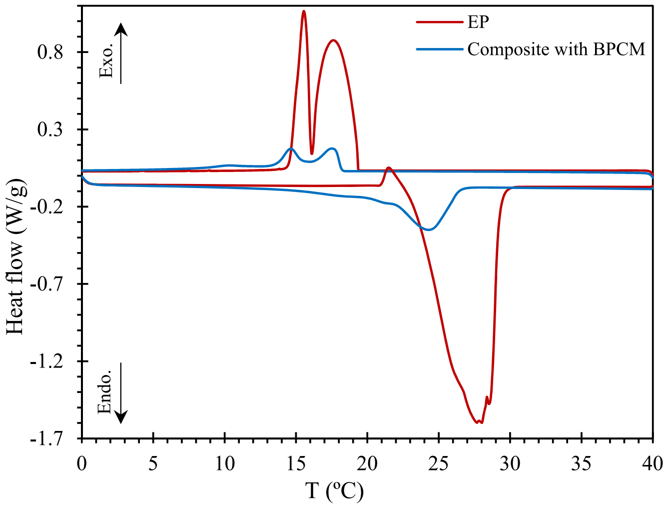

Fig. 7. DSC thermograms obtained for EP and composite with BPCM.

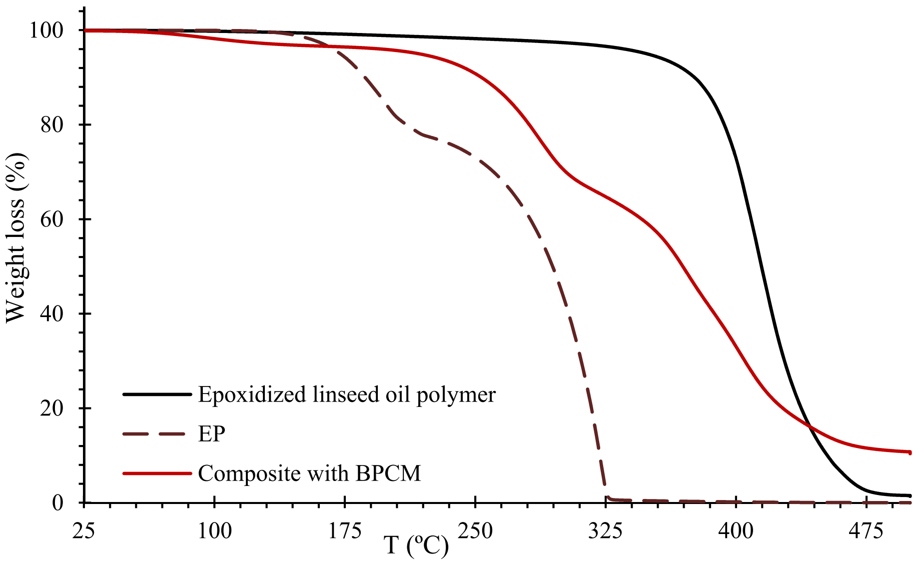

Fig. 6. TGA curves for pure EP, epoxidized linseed oil polymer and the composite with BPCM.

Both melting and freezing points of the composite occur at lower temperatures compared to pure EP and slightly more incongruency is also observed. The heat flow and enthalpy measured for the composite with BPCM is lower than that of the pure BPCM (EP), as the proportion of BPCM in the composite were ca. 25%. The measured latent heat of fusion for BPCM with DSC was 183 J/g, but it was reduced to 45 J/g after incorporation into the composite. Similar trend was reported in the literature [10,11], when a reduction in latent heat of fusion after incorporation of BPCMs into wooden materials and composite was observed. Furthermore, a correlation between the latent heat of fusion and the amount of impregnated PCM and temperature shift in onset and endset were reported.

Fig. 8 shows the T-history profile for the composite with and without BPCM, EP (BPCM) and reference (Cu) during the cooling (8a) and heating process (8b). The measured ambient temperatures were constant throughout the experiments with ± 0.8 °C maximum deviation. Once placed in the climate chamber at 0 °C, the composites, BPCM and the reference's temperatures decrease gradually from the starting temperature at 40 °C and continues to decease with time until it reaches the chamber's ambient temperature (0 °C). During the cooling, phase change transition was observed for BPCM starting at 20 °C, but due to some degrees of supercooling, it fully solidified at 21.7 °C. However the composite with BPCM does not experience supercooling but some incongruencies occurs during the cooling process and also the freezing point of the composite starts at lower temperature (19 °C) and fully solidifies at 12 °C.

T-history measurements showed that, during the heating process, the pure BPCM melts congruently at 24.7 °C, and the issue related to polymorphism is not observed compared to DSC measurements. Furthermore, the composite hosting BPCM experience incongruent melting with slight decrease in melting temperature and two melting points at around 18 °C and 23 °C were observed.

During the cooling and heating processes (Fig. 8), the composite without BPCM reached the equilibrium faster compared to Cu plate and composite hosting BPCM, due to lower thermal mass (heat capacity, mC_p) of the composite without BPCM. The temperature profile of the materials in transient conduction condition (Eq. (7)) is a function of thermal mass of the materials (mC_p). Increment in (mC_p) leads to more energy absorption and storage by the material during heating, and release more energy during cooling process, resulting in delay for reaching the ambient temperature. This shows that incorporation of the BPCM in the composite significantly improves the thermal mass of the material enabling it to absorb and store excess energies when it is available.

Fig. 9 shows the specific heat capacity for EP (BPCM), the composite with and without BPCM calculated using Eq. (9) during cooling and heating processes. The measured heat capacity of the composite without BPCM is ca. 2 J/g K, which is slightly higher than that of solid wood reported in the literature [10,11]. This is because the specific heat capacity is not dependent on the density and the species, and this slight increment is probably due to the effect of the used epoxidized linseed oil polymer on the specific heat capacity. After incorporation of BPCM, the composite with BPCM possess a specific heat capacity at around 4–5 J/g K attributed to the specific heat capacity of the BPCM.

Fig. 10 illustrates the measured enthalpy for EP, the composite with and without BPCM during cooling and heating process. The results show that the composite without BPCM follows a pattern similar to solid wood [10,11], in which the composite does not experience storing and releasing energy in terms of latent heat and the energy is stored and released as sensible heat during the heating and cooling courses. After incorporation of BPCM in the composite, the composite shows latent heat storage during phase transition, while before and after phase transition, the storage and releasing of energy occur in terms of sensible heat. The latent heat of pure BPCM measured with T-history is around

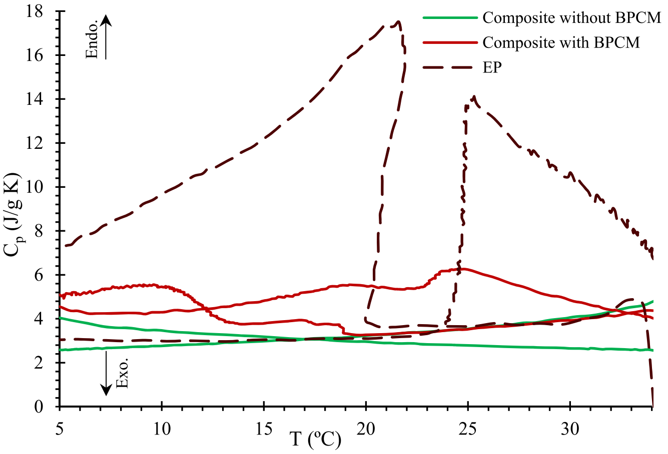

Fig. 9. Melting and freezing specific heat capacity for composite samples and BPCM (EP).

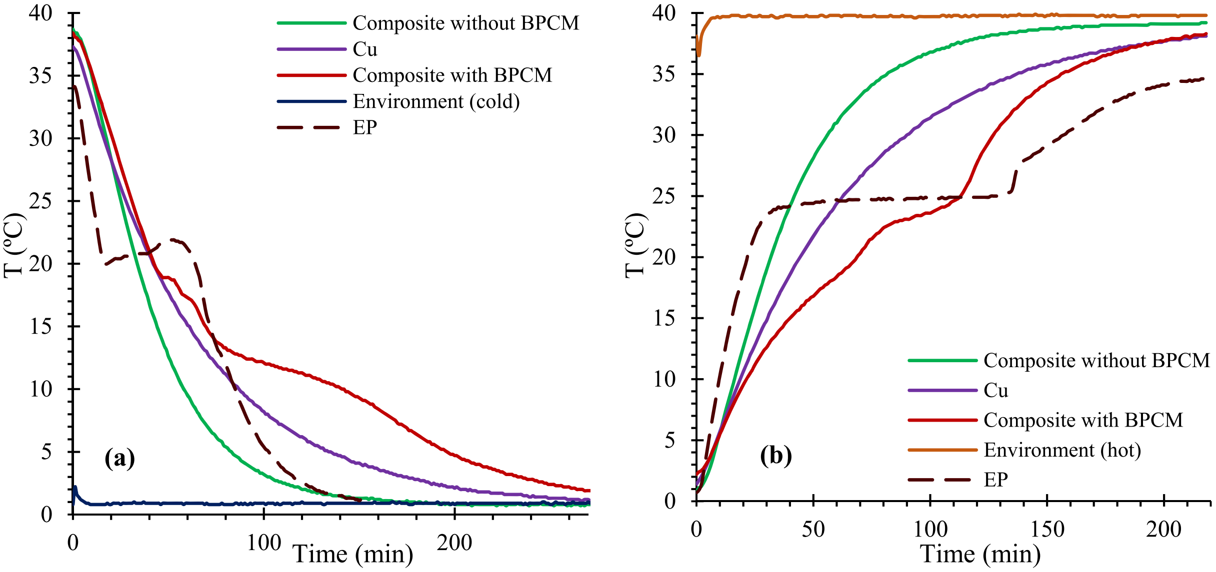

Fig. 8. T-history curves over cooling/heating cycle for (a) cooling and (b) heating.

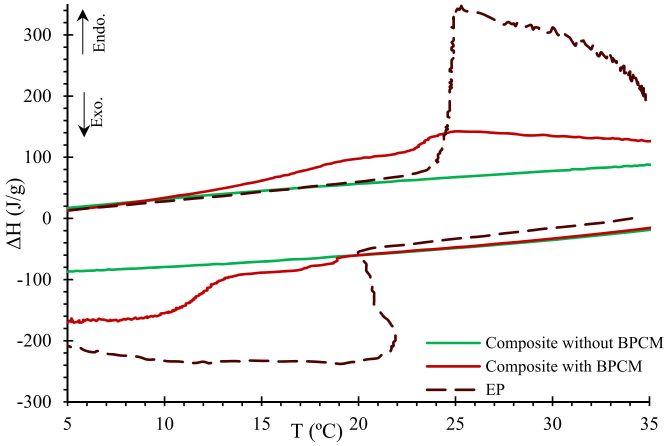

Fig. 10. Melting and freezing enthalpy for composite samples and BPCM (EP).

200 J/g, and it reduces to ca. 50 J/g when around 25% of the composite consists of the BPCM.

The pattern of thermal properties of tested samples with DSC and T-history are similar. However, DSC displays details related to polymorphic nature of fatty acid esters at the melting peak point while it cannot be detected by the T-history. T-history method used large samples that cooled down naturally in the chamber and thus, the results are more reliable compared to the DSC where a small sample was analyzed.

Fig. 11 shows thermal cycling behavior of the composite with and without BPCM inside two similar small cubes. The test was run inside a climate chamber with temperatures oscillating between 0 and 40 °C. The temperature inside the climate chamber and inside the cubes were monitored over time. The sensors inside the cubes do not touch the composites and they only record the temperature of the environment inside the cubes. The results show that the efficiency of using the composite with BPCM is obvious. After almost one week intensive cooling and heating processes, the composites with BPCM were expected to show certain changes due mainly to possible leakage of the BPCM but the results show that although there might be some degrees of leakage, the thermal behavior of the composites with BPCM did not undergo changes showing that the possible leakage was not significant. It is observed that the temperature inside the cube without BPCM changes significantly faster than that in the cube with BPCM. The cube with BPCM resists better to the temperature fluctuations of the environment and when the ambient temperature increase, extra energy is absorbed by the composites with BPCM and released during the cooling keeping the temperature inside the cube more constant. The environment temperature changes from 0 to 40 °C provokes temperature changes from 13 to 28 °C in the cube with BPCM that can be compared to the range between 4 and 38 °C in the cube without BPCM.

4. Conclusions

Novel bio-based composite with energy function have been developed by combining wood particles, BPCM and plant oil as renewable resources. The main findings of the study are summarized as follow:

- Sawdust particle reinforced composite showed optimal performance when 25% ester is impregnated in the composite and this proportion ensures that the problem of leaching is negligible.
- Moisture absorption and desorption tests showed that the composites without BPCM absorbed and desorbed more moisture compared to those with BPCM. Based on the data from moisture absorption and desorption tests, MBV was calculated as 2.07 g/m^2 RH% for the composites with BPCM and 3.2 g/m^2 RH% for the composites without BPCM, thus showing that the MBV for both types is higher than 2 g/m^2 RH% and within the range of excellent category, according to the Nordtest protocol.

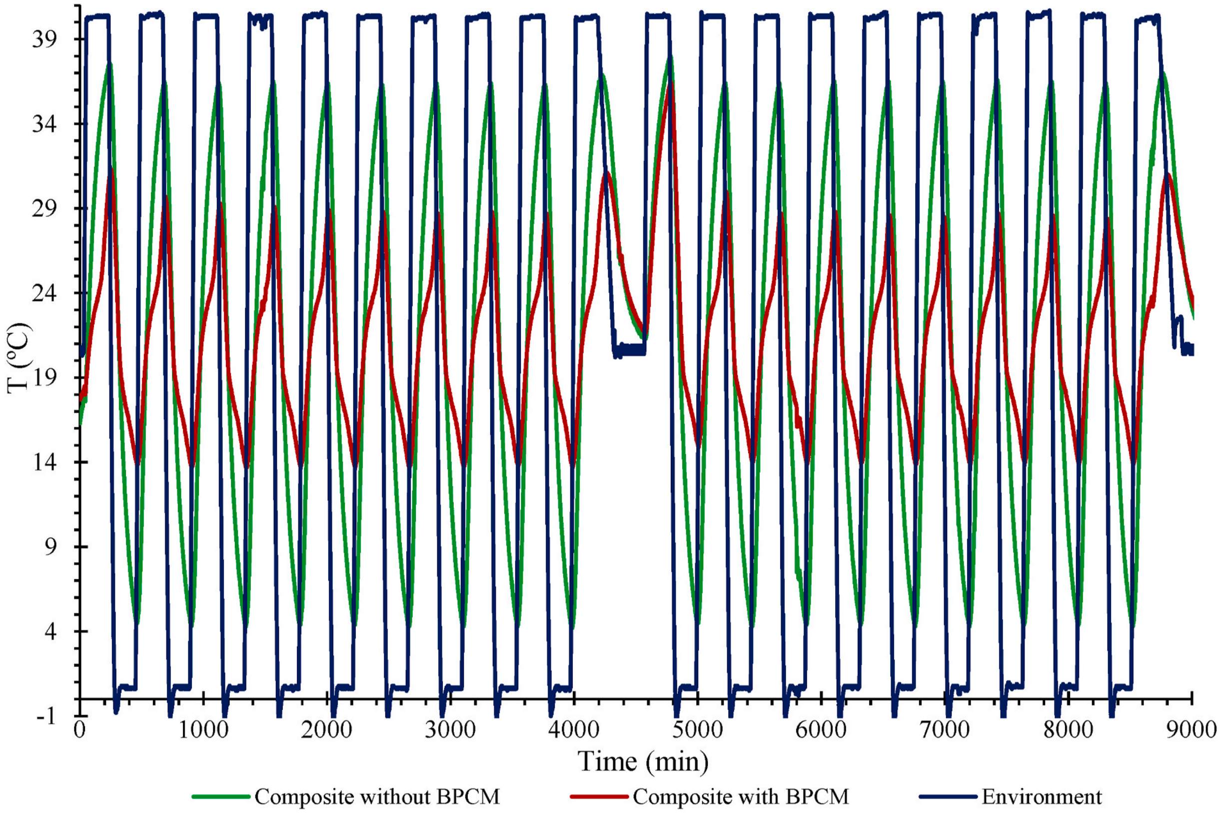

Fig. 11. Difference in the thermal cycling behavior of the composites in the test cubes.

- Thermal stability of the composite was tested with thermogravimetric analysis showing that the ester is thermally stable up to 150 °C, the epoxidized linseed oil polymer is a stable binder up to 340 °C. The composite is thermally stable up to 200 °C.
- DSC results showed that there is some changes at the melting peak point, which are probably related to polymorphism character of ester. The results for the composite underwent some shifts to lower temperatures for both melting and freezing temperatures; also, the enthalpy of the composite is proportional to the amount of ester in the composite.
- Thermal characterizations of the composites with and without BPCM were conducted with T-history method. Results showed that the composite with BPCM had significant thermal mass, ability to store excessive energy in terms of latent heat and keep the temperature constant for longer time. The specific heat capacity of the composite with BPCM was 4–5 J/g K i.e., higher than that of without BPCM of ca. 2 J/g K. In terms of latent heat of fusion the BPCM (EP) has high latent heat at around 200 J/g, however the composite with BPCM containing 25% BPCM, has latent heat of fusion at around 50 J/g, while that without BPCM has no latent heat.
- Thermal cycling test was conducted in small prototype cubes, concluding the effect of thermal mass when the cube made of the composites with BPCM could deal with temperture fluctuation much more effecient compared to that without BPCM, and the result showed a stable thermal behaviour after the temperature cycling.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The study has been carried out within the framework of Smart Energy Systems Research and Innovation Program (ERA-Net E2B2) in the project “Bio-Based Phase Change Materials Integrated into Lignocellulose Matrix for Energy Store in Buildings (BIO-NRG-STORE)”. The work was funded by the Swedish Energy Agency (Energimyndigheten) (project nr. 50298-1).

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Nomenclature

A: Heat transfer area [m^2]
c_p: Specific heat [J/g K]
H: Enthalpy [J/g]
m: Mass of the samples [kg]
Q: Heat [W]
T: Temperature [°C]
t: Time [s]

u: Overall heat transfer coefficient [W/m^2 K]

Greek symbol

Δ: Difference
∞: Ambient

Abbreviations

BPCM: Bio-based phase change materials
ELO: Epoxidized linseed oil
EP: Ethyl palmitate
DSC Differential scanning calorimetry:
PCM: Phase change materials
Subscripts:
f: Final
i: Initial
max: maximum
min: minimum
n: Time point
ref: Reference
samp: Sample