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Name and Surname

Muhammad Faisal Junaid

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Submitter: Muhammad Faisal Junaid, MSc.
Department of Materials Engineering and Physics
Faculty of Civil Engineering, STU in Bratislava
Radlinského 11, SK-810 05 Bratislava, Slovakia

Supervisor: Prof. Dr. Igor Medveď
Department of Materials Engineering and Physics
Faculty of Civil Engineering, STU in Bratislava
Radlinského 11, SK-810 05 Bratislava, Slovakia

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prof. Ing. Stanislav Unčík, PhD.
Dean of Faculty of STU

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1 Introduction

1.1 Background and significance

Phase change materials (PCMs) are effective for thermal energy storage due to their ability to absorb and release heat during phase transitions. These materials can regulate temperature fluctuations in buildings, reducing the need for heating and cooling, thus improving energy efficiency. While biobased organic PCMs are widely used for their thermal and chemical stability, meanwhile challenges such as leakage and low thermal conductivity hinder their broader application in construction materials. When incorporated directly into cementitious materials e.g., mortar, PCMs can cause leakage, which disrupts the hydration process of cement and reduces the overall effectiveness of the material. To address these issues, shape-stable composite PCM has been developed. This composite uses porous supporting material, such as activated carbon, to retain PCM within its porous structure and prevent leakage. The supporting material typically features various-sized pores, which help absorb and contain the PCM through adsorption or surface tension. Activated carbon derived from coconut shells (AC_{cs}) has several advantages including high porosity, a large surface area, and excellent thermal conductivity. When impregnated with PCM, this material can efficiently store and release thermal energy during the melting and solidifying phases.

Furthermore, the integration of shape-stable composite PCM (AC_{cs}/PCM) into cementitious materials offers a passive thermal energy storage solution for buildings. By adding this composite to cement mortar, it can absorb heat during the day and release it at night, providing a passive solution for heating and cooling buildings. This approach reduces the need for traditional HVAC systems, thus improving energy efficiency and lowering energy costs. Moreover, the use of AC_{cs}/PCM composites can enhance indoor thermal comfort by maintaining stable temperatures. In particular, activated carbon derived from coconut shells is an ideal support material due to its high porosity and ability to retain significant amounts of PCM. Composite PCM, made by AC_{cs}/PCM, offers a sustainable and efficient solution for building materials that require thermal regulation. The potential benefits of using AC_{cs}/PCM composite in building materials include energy efficiency, increased comfort and a reduction in carbon emissions. However, achieving optimal performance requires careful consideration of the composite's properties and application requirements. The study represents an innovative approach to waste utilization and energy conservation contributing to sustainability and economic value by turning agricultural waste into a valuable resource for building materials.

1.2 Research objectives

It is crucial to develop biobased materials for energy applications with the aim of building a more sustainable future. The future energy supply chain will integrate various renewable energy sources alongside advanced engineering and material innovations for energy efficiency, storage, and conservation. There is a need for bioderived PCM that is non-corrosive and cost-effective with stable thermal and chemical characteristics.

In agreement with the individual research plan of my doctoral study, the thesis includes both basic and practical objectives aimed at comprehending the properties of potentially efficient form stable composite biobased PCM. Specifically, the main objectives of this thesis are:

- To provide useful guidance for selecting appropriate materials and propose cost-effective and sustainable method of biobased PCM integration for different construction applications considering the circular economy paradigm.
- To evaluate the potential of waste coconut shell as a support material in carbonized form for shape stabilization and thermal conductivity enhancement of novel biobased PCM to establish new environment-friendly utilization areas for it.
- To engineer a powerful carrier framework for the preparation of leakproof shape stable composite biobased PCM capable of efficient heat storage with desirable environmental characteristics.
- To manufacture thermally efficient and thermally enhanced cement mortar containing composite biobased PCM for optimized thermoregulation performance in sustainable building envelopes.

1.3 Scope of the study

In a building structure, there are several techniques to ensure that PCMs remain stabilized. Two common methods are shape stabilization (where PCMs are integrated with supportive materials to maintain their form) and encapsulation (micro- or macro-encapsulation). Even though microcapsule PCMs are possibly utilized for latent energy storage in buildings, their practical application is prohibitively expensive because a typical building requires a relatively large quantity of PCMs. This necessitates the development of low-cost materials and synthesis techniques.

The most challenging task is finding proper PCM carriers that are not only compatible with building materials but also have a high absorption capacity while preventing PCM leakage. In literature, only a few eco-friendly agricultural waste materials have been used as carrier material, e.g., waste wood, corn cob, palm kernel shell, lemon peel derived activated carbon for effective shape stabilization and their subsequent utilization to manufacture composite energy storage building materials. However, these materials exhibit several limitations that hinder their effectiveness in TES applications.

In addition, the promotion of the widespread application of biobased PCMs in the construction sector not only requires more specific research on resolving inherent drawbacks and improving integration technologies with building elements but also on economic, demand-supply, comparative and real-scale performance analyses of biobased PCMs. Thus, the research will help in the selection of the suitable, cost-effective and green supporting material for shape-stable composite biobased PCM and its subsequent integration with effective thermally enhanced cement mortar for optimized thermoregulation performance in buildings.

2 Materials and methods

2.1 Material selection

PCM. For the preparation of eutectic mixture (EPCM) natural Food Chemicals Codex-Food grade CA (chemical formula: $CH_3(CH_2)_8COOH$; purity: ≥98%; density: $0.893\ g{\cdot}ml^{-1}$ at 25 °C, T_m: 27 – 32 °C) and MA (chemical formula: $CH_3(CH_2)_{12}COOH$; purity: ≥98%; density: $0.90\ g{\cdot}ml^{-1}$, T_m: 56 °C) were procured from Merck and Carl Roth GmbH, respectively.

Supporting Material. Food-grade powdered activated carbon (YZ-400C) subjected to steam activation at a temperature exceeding 900 °C made from coconut shell waste was procured from a commercial supplier (Zhengzhou Yihang Water Purification Materials Co., Ltd. China).

Cement. The cement used for the mortar production was CEM V/A (S-P) 42.5R complies with EN 197-1 sourced from Cementerie Aldo Barbetti S.p.A., Italy.

Fine aggregate. Fine alluvial sand with grain size designation 0/3 mm was procured from Calcestruzzi Cipiccia S.p.A. aggregate production plant located in Narni (TR), Italy conforming to the EN 12620 and EN 13043 standards.

2.2 Preparation process

Activated Carbon. Coconut shells were subjected to pyrolysis at 500°C followed by steam activation at a temperature exceeding 900°C to obtain activated carbon with high porosity and enhanced absorption capacity.

Eutectic PCM. The objective of the current study was to create a eutectic mixture of CA and MA with a phase change temperature of 21 °C, i.e., suitable for building applications [1–4]. Among the tested proportions, the optimal ratio was found to be 72.5 wt.% CA to 27.5 wt.% MA.

Vacuum Impregnation: AC_{cs} was vacuum treated to absorb EPCM ensuring a maximum retention of 80% PCM. This process enabled uniform distribution of EPCM within the porous structure improving its phase change properties.

Cement mortar production. To manufacture thermally efficient cement mortars (TECMs), a portion of the sand was replaced with AC_{cs}/EPCM composite at varying weight percentages of 10%, 20% and 30%. The mortars prepared with these substitutions were labeled as TECM-10%, TECM-20% and TECM-30%, respectively (Table 2.1).

Table 2.1: Mixture proportions

Material	**Cement (g)**	**Sand (g)**	**Water (g)**	**AC_{cs}/EPCM composite (g)**
Control	450	450	337.5	0
TECM-10%	450	405	337.5	45
TECM-20%	450	360	337.5	90
TECM-30%	450	315	337.5	135

2.3 Experimental analysis

Chemical characterization. X-ray diffraction analysis and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT-FTIR) were used to assess the type of interaction between EPCM and AC_{cs}.

TES properties: Differential scanning calorimetry (DSC) was used to assess energy storage capacity.

Thermal stability. The long-term thermal stability was evaluated through repeated thermal cycling and subsequent DSC measurements after 10, 100, 500 and 1000 thermal cycles. To investigate thermal degradation performance, TGA was performed with an upper limit of 500 °C.

Thermal properties. Thermal conductivity apparatus was used to assess the thermal conductivity of composite PCM along with corresponding melting and crystallization time to yield T-history curves. Moreover, the thermal conductivity of mortar samples was measured using the Hot Disk TPS 2500S instrument from Hot Disk AB through the Transient Plan Source (TPS) method.

Mechanical Properties: Compressive strength tests were conducted according to ASTM C109 standard to determine the structural integrity of mortar samples containing the composite PCM.

Thermoregulation Performance: Mortar panels were subjected to controlled heating and cooling cycles to assess temperature variations and heat dissipation behavior.

3 Key Findings

3.1 Chemical characterization

3.1.1 XRD analysis

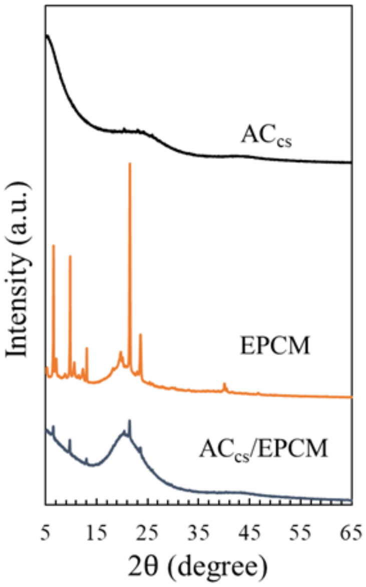

Figure 3.1: XRD analysis results

Figure 5.7 presents the XRD analysis results of AC_{cs}, EPCM, and AC_{cs}/EPCM. The results indicate that AC_{cs} has an amorphous nature, exhibiting a non-crystalline structure. In contrast, EPCM shows a crystalline structure with distinct peaks at 6.5°, 9.8°, 13.0°, 21.5°, 23.6°, and 40.0° 2θ angles. These peaks are associated with the unique crystalline structure of EPCM resulting from the amalgamation of CA and MA. Meanwhile, AC_{cs}/EPCM retains some of the amorphous characteristics of ACcs for most of the XRD curve while also showing peaks around 6.4°, 9.6°, 13.0°, 21.5°, and 23.6° 2θ angles, similar to those of EPCM. This reinforces the evidence of successful impregnation of EPCM into the ACcs matrix. However, the peak intensity is slightly reduced, and some peaks are absent in AC_{cs}/EPCM compared to EPCM, likely due to some shadows imparted by AC_{cs} on the EPCM crystal structure.

3.1.2 DRIFT-FTIR

It can be clearly observed that all primary absorption bands of EPCM remain evident in the spectra of AC_{cs}/EPCM composite with no significant shifts in wavenumber positions. This stability in peak locations suggests the structural integrity of EPCM is maintained within the composite matrix. Furthermore, no new absorption peaks appear in spectra aside from the characteristic bands associated with both the EPCM and ACcs framework. This lack of additional peaks confirms that the interaction between the EPCM and ACcs is primarily physical with no chemical interaction occurring between them. This successful integration of EPCM into the ACcs framework is therefore demonstrated as the composite retains the distinct spectral features of both materials such as C–H, C=C, C=O, and C–O (see Fig. 3.2a).

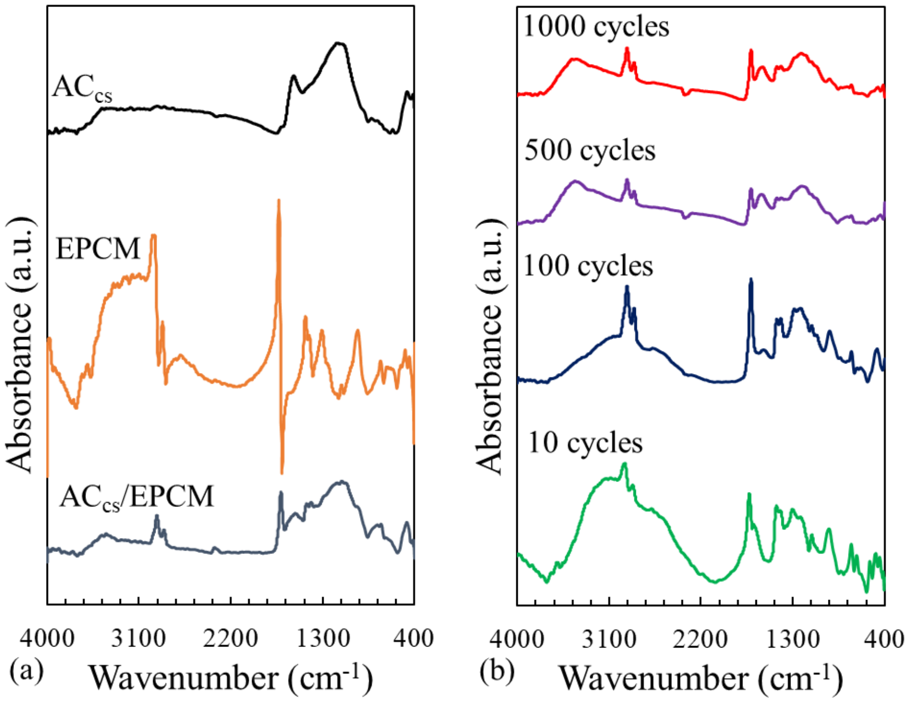

Figure 3.2 FTIR spectra (a) studied materials; (b) thermal cycling of AC_{cs}/EPCM

Additionally, FTIR analysis was also conducted after 10, 100, 500 and 1000 melting-crystallization cycles to evaluate the durability and chemical stability of the developed composite (see Fig. 3.2b). Spectral analysis conducted after thermal cycles showed that the composite retained spectral profiles highly consistent with those observed prior to cycling. This consistency across repeated thermal cycling highlights the chemical stability of the composite. Despite an extensive thermal cycling process, no signs of physicochemical degradation were observed. This indicates that the ACcs framework extensively supports the EPCM and prevents any leakage or deterioration. Thus, the composite sustained its structural and functional integrity over prolonged thermal cycling.

3.2 DSC

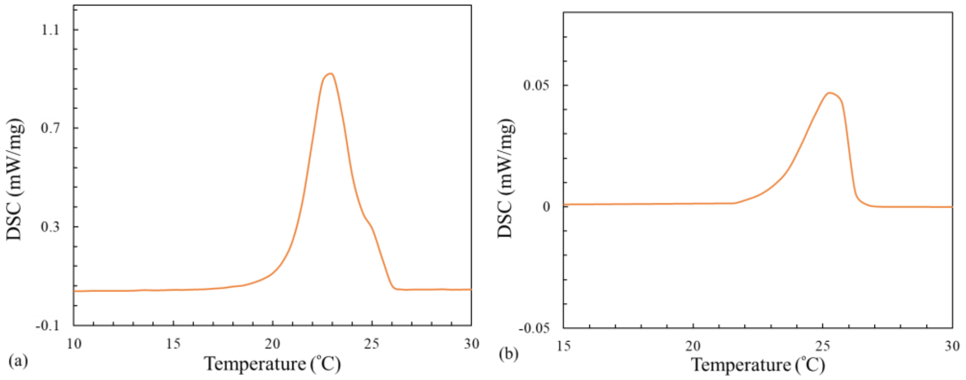

Figure 3.3: Melting temperature curves (a) EPCM; (b) AC_{cs}/EPCM

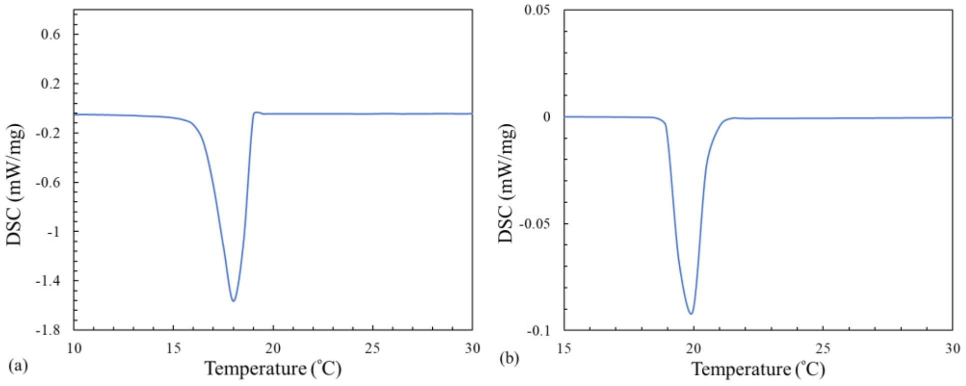

Figure 3.4: Crystallization temperature curves (a) EPCM; (b) AC$_{\text{cs}}$/EPCM

The resulting melting-crystallization curves are shown in Figs. 3.3–3.4 and Table 3.1 contains all DSC data for the corresponding samples. The curves present endothermic and exothermic peaks originating from the phase transition (melting and crystallization, respectively) of samples. Based on these distinctive peaks, the onset melting temperature (T_{startM}) of EPCM was determined to be 20.5 °C and the onset crystallization temperature (T_{startC}) was measured to be 19.0 °C.

Furthermore, the melting and crystallization temperatures of the AC$_{\text{cs}}$/EPCM composite were measured to be 21.8 °C and 19.1 °C, respectively (see Table 3.1). The finding also confirmed a marginal difference in the phase transition temperature of AC$_{\text{cs}}$/EPCM composite, i.e., a small increase in T_{startM} and T_{startC}. This phenomenon can be explained by different factors, such as the confinement effect and physical interaction. During melting and crystallization, the porous structure of AC$_{\text{cs}}$ severely restricts the movement of long chains of EPCM molecules and their easy entanglement within AC$_{\text{cs}}$ pores. This confinement causes the melting and crystallization of the solid and molten molecular chains, respectively, to occur at a higher temperature [5]. Also, this slight increase in T_{startM} for composite indicates the enhanced thermal conductivity which facilitates more effective heat conduction favoring the melting process to occur homogeneously [6].

Melting enthalpy (ΔH_M) and crystallization enthalpy (ΔH_C) of EPCM and AC$_{\text{cs}}$/EPCM were found to be 157.2 J/g and 156.3 J/g, and 32.5 and 32.6 J/g, respectively (see Table 3.1). These findings confirm the efficacy of AC$_{\text{cs}}$ as a carrier material for shape-stabilized biobased PCM owing to its marginal variation in latent heat during melting and crystallization [7].

Table 3.1: DSC results of EPCM and AC$_{\text{cs}}$/EPCM composite

Material	**T_{startM} (°C)**	**T_{peakM} (°C)**	**T_{endM} (°C)**	**ΔH_M (J/g)**	**ΔH_C (J/g)**	**T_{startC} (°C)**	**T_{peakC} (°C)**	**T_{endC} (°C)**
EPCM	20.5	22.5	24.4	157.2	156.3	19.0	18.5	17.1
AC$_{\text{cs}}$/EPCM	21.8	23.8	25.8	32.5	32.6	19.1	18.2	17.3

3.3 Thermal stability

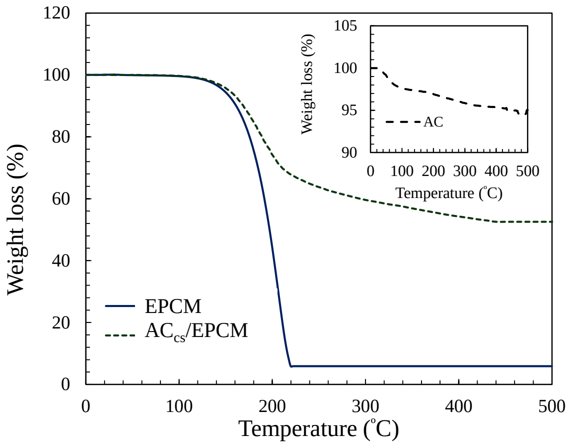

Figure 3.5: TGA curves of AC_{cs}, EPCM and AC_{cs}/EPCM

The AC_{cs}/EPCM composite followed a similar trend to EPCM demonstrating a one-step process of thermal decomposition. However, the ACcs/EPCM composite retained 53% of its mass at 500 °C. This is because only EPCM (47 wt%) thermally decomposed while AC_{cs} remained relatively unaffected. Therefore, the thermal stability of AC_{cs}/EPCM composite outlines the suitability for its use up to 155 °C (see Fig. 3.5). This temperature is significantly higher than its usual operating temperature, which can be outlined by the onset melting temperature of EPCM (i.e., ~ 21 °C). Such high thermal stability suggests that the composite can effectively retain its thermal characteristics under normal operating conditions while ensuring structural integrity. This capability is crucial for applications where consistent performance is required even when exposed to varying thermal conditions.

3.4 Thermal reliability

3.4.1 Melting

Figures 3.6-3.8 present the thermal cycling results of the melting phase which indicate that T_{startM} of the EPCM shows slight fluctuation initially but remains relatively stable beyond 500 cycles. The temperatures T_{peakM} and T_{endM} show some variations particularly at higher cycle numbers with T_{endM} increasing to 27.07 °C by 1000 cycles. The melting enthalpy ΔH_M slightly drops (~2.2 %) from 157.9 J/g at 10 cycles to 154.4 J/g at 1000 cycles indicating a minor loss in the energy storage capacity as the material undergoes more phase transitions through repeated cycling. Thus, the EPCM displayed excellent stability against thermal cycling even up to 1000 cycles with small variations (~ 2 %) in both the melting temperature and melting enthalpy values (see Figs. 3.6 and 3.8).

For AC_{cs}/EPCM, a slight increase in phase change temperatures was observed by 1000 thermal cycles (see Fig. 3.7). This behavior is similar to that of AC_{cs}/EPCM at zero cycles. The melting temperature T_{startM} increased from 21.8 °C to 22.3 °C and T_{peakM} increased from 23.8 °C to 27.5 °C indicating the material requires higher temperatures to melt as cycling progresses (see Figs. 3.7 and 3.8). The melting enthalpy ΔH_M decreases from 32.5 J/g to 31.2 J/g, reflecting a small loss in the composite's latent heat storage capacity. It is likely due to degradation or a minor EPCM loss from the composite with thermal cycling [8].

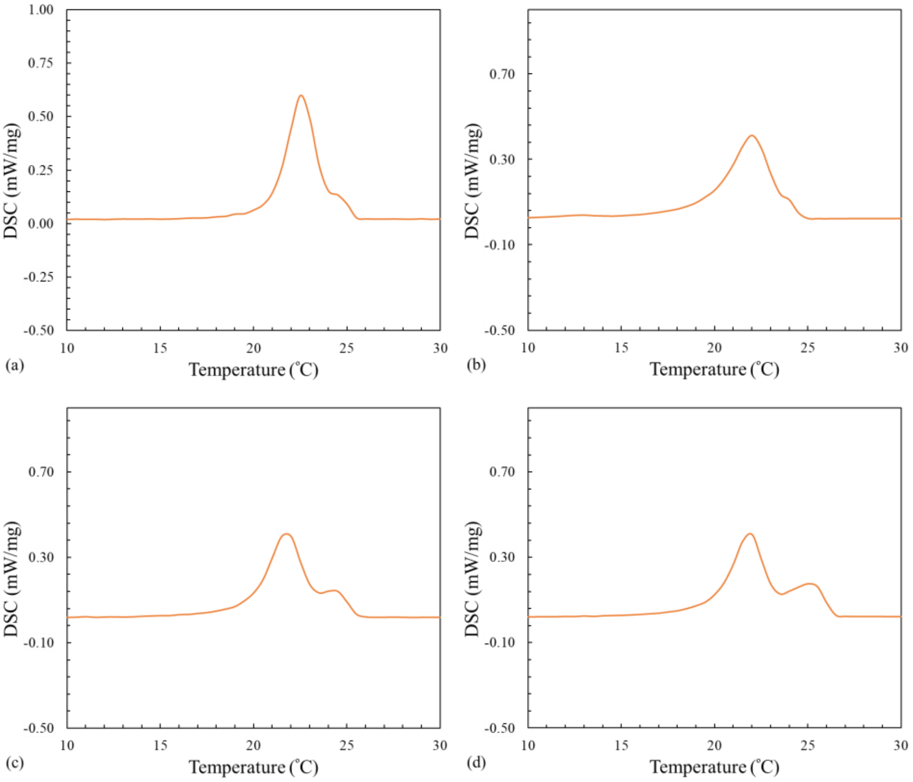

Figure 3.6: Melting temperature curves of EPCM after thermal cycling (a) 10 cycles; (b) 100 cycles; (c) 500 cycles; (d) 1000 cycles

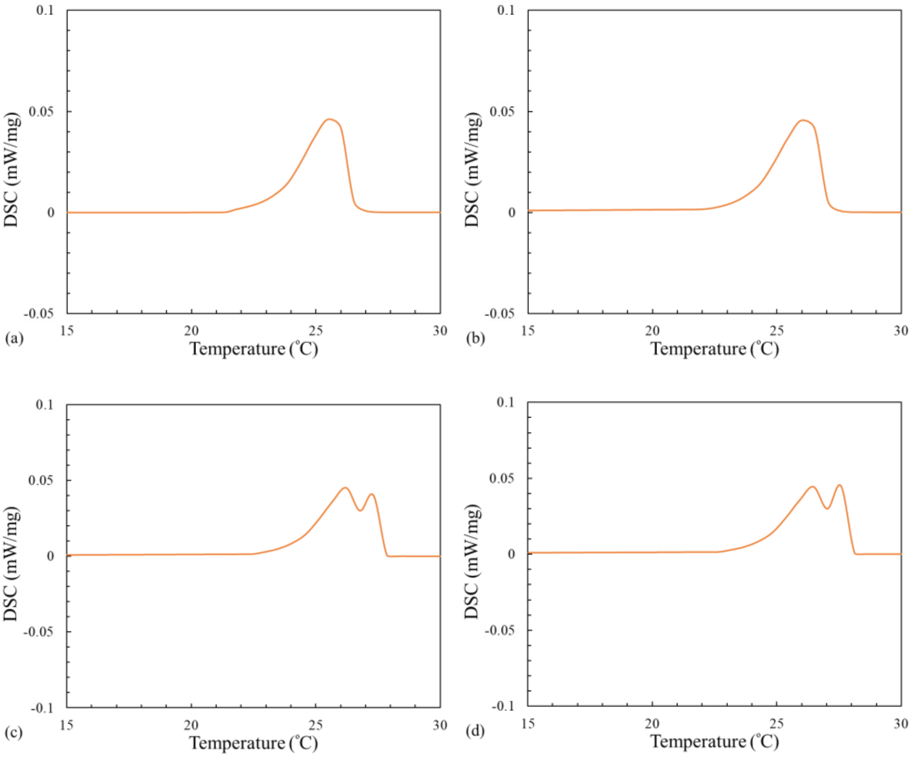

Figure 3.7: Melting temperature curves of AC_{cs}/EPCM after thermal cycling (a) 10 cycles; (b) 100 cycles; (c) 500 cycles; (d) 1000 cycles

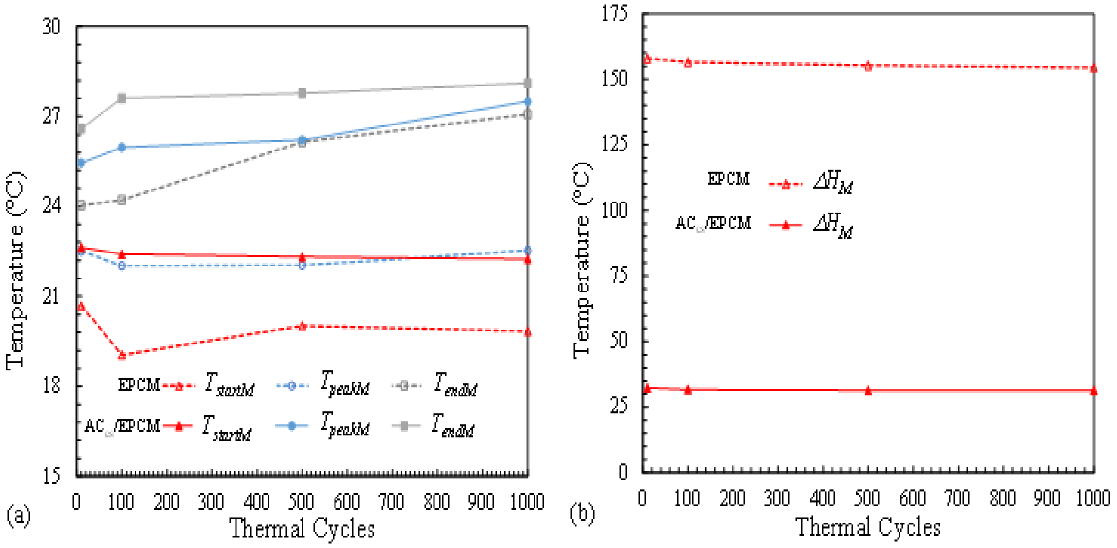

Figure 3.8: Melting phase characteristics of EPCM and AC$_{cs}$/EPCM: (a) temperatures; (b) enthalpy

3.4.2 Crystallization

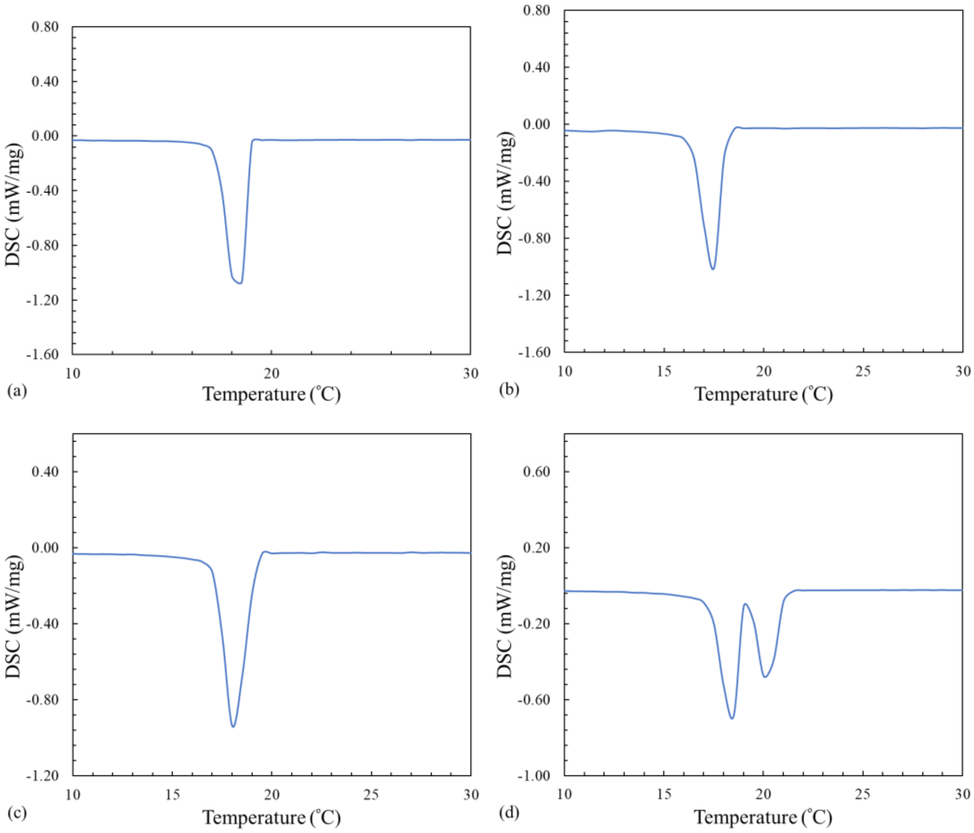

Figure 3.9: Crystallization temperature curves of EPCM after thermal cycling (a) 10 cycles; (b) 100 cycles; (c) 500 cycles; (d) 1000 cycles

Figures 3.9-3.11 present the thermal cycling results of EPCM and AC$_{cs}$/EPCM. For EPCM, T_{startC} increases slightly from 19.0 °C to 21.5 °C by 1000 cycles, while T_{peakC} and T_{endC} also shift upwards (see Fig. 3.9). There is also a slight drop in ΔH_C similar to

ΔH_M. Several researchers studied fatty acids-based EPCM mixtures and observed similar variations in phase transition (melting/crystallization) temperatures during thermal cycling [8,9]. These variations in transition temperatures and losses of enthalpy mainly occur because PCM components experience degradation and/or due to the presence of impurities in the fatty acids-based bio PCMs that are used to prepare eutectic mixtures. Moreover, long-term thermal cycling can induce molecular rearrangements or phase separation. After long-term thermal cycling, a PCM undergoes subtle changes in its molecular structure favoring slight variations in its phase transition behavior [10].

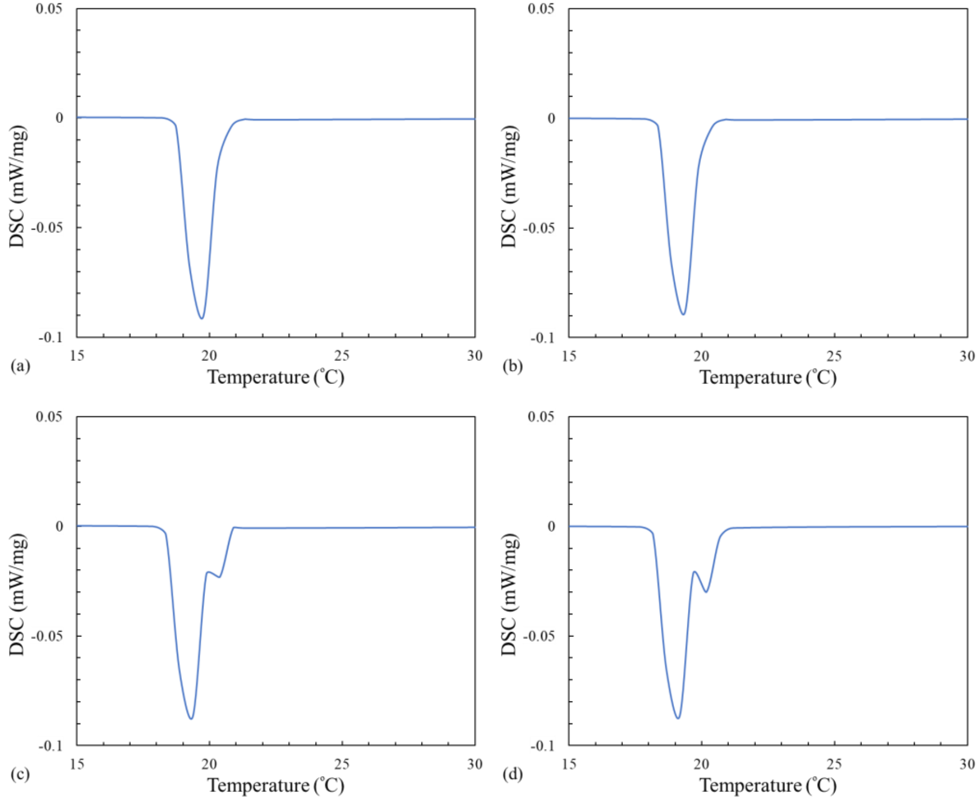

Figure 3.10: Crystallization temperature curves of AC_{cs}/EPCM after thermal cycling (a) 10 cycles; (b) 100 cycles; (c) 500 cycles; (d) 1000 cycles

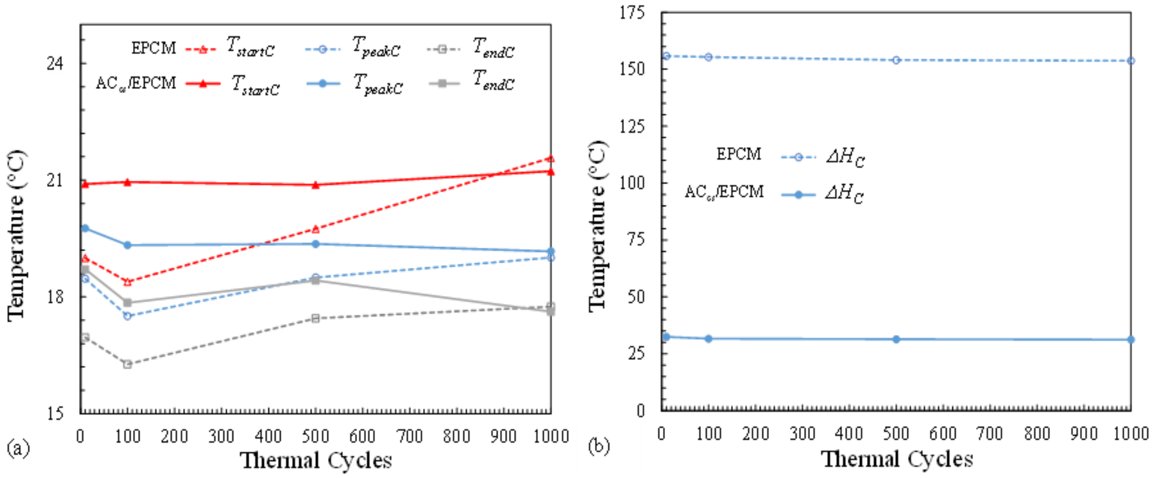

Figure 3.11: Crystallization phase characteristics of EPCM and AC_{cs}/EPCM: (a) temperatures and (b) enthalpy

For AC_{cs}/EPCM, the crystallization process also experiences minor shifts in temperature after 1000 cycles with T_{startC} increasing from 19.1 °C to 21.2 °C and T_{peakC} rising from 18.2 °C to 19.1 °C (see Fig. 3.10). The ΔH_C decreases slightly from 32.6 J/g to 31.2 J/g (see Fig. 3.11). The rise in crystallization temperatures could be associated with an improved nucleation efficiency over time as repeated cycling favors the stabilization of EPCM within AC_{cs}. However, a minor decrease in ΔH_C suggests some molecular rearrangements or slight aging of the EPCM leading to a slightly reduced capacity to release stored heat during crystallization. A similar trend was also observed by Zhang et al. [9] for a shape-stabilized EPCM comprising expanded graphite as a carrier material. Thus, the variations in thermal characteristics observed in the current study align with the existing literature and constitute reliable biobased composite material for TES in building applications.

3.5 TES characteristics of composite PCM

Thermal conductivity is an important consideration for selection of PCMs and preparing composite PCMs. Literature manifests that lower thermal conductivity can prolong the time required for storing and releasing latent heat. Therefore, it is essential to enhance the thermal conductivity of the composite PCMs, enabling them to be used in various practical implications. Figure 3.12 represents the thermal conductivity of EPCM and AC_{cs}/EPCM. The thermal conductivity of AC_{cs}, EPCM and AC_{cs}/EPCM were determined to be 0.49, 0.17 and 0.30 W/mK, respectively. The findings revealed that the AC_{cs}/EPCM's thermal conductivity is about 43% higher than EPCM and 38% lower than AC_{cs}. It can be concluded that the carbon matrix present within the porous structure of AC_{cs} offers numerous pathways for heat conduction. In fact, the thermal conductivity of AC_{cs} is insufficient to potentially provide such an increase in the thermal conductivity of EPCM. Although AC_{cs} has a porous structure filled with air which has a low thermal conductivity (i.e., 0.026 W/mK) [11], it significantly enhances the thermal conductivity of EPCM [12].

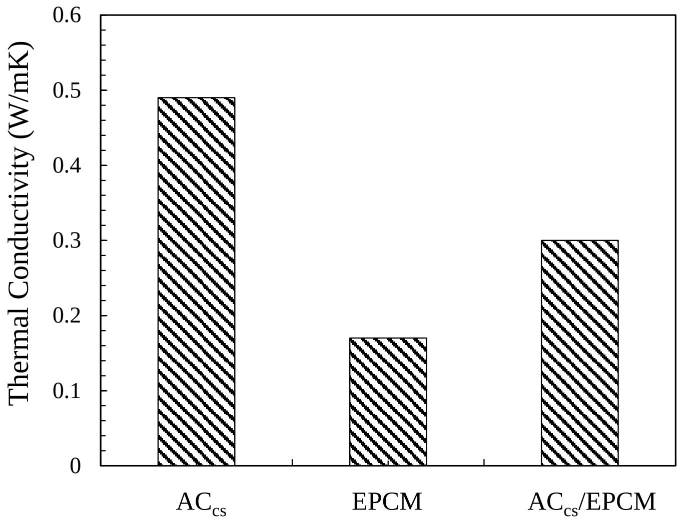

Figure 3.12: Thermal conductivity results

Figure 3.13 represents the T-history curves showing the temperature changes over time. Phase transition time was defined as the amount of time required to complete phase transition (melting/crystallization) while maintaining a nearly constant temperature. It was observed that the melting time for EPCM and AC_{cs}/EPCM was determined to be 648 sec and 417 sec, respectively. The result clearly demonstrates the reduction (~ 35%) in melting time of EPCM in AC_{cs}-based composite. In a similar pattern, there was a reduction of time (~30%) required for crystallization of AC_{cs}/EPCM (454 sec) as compared to EPCM (651 sec) thereby confirming the enhanced thermal conductivity of composite material. Therefore, the reduction in both melting/crystallization times confirms the improved thermal conductivity of EPCM within the scaffold of AC_{cs}.

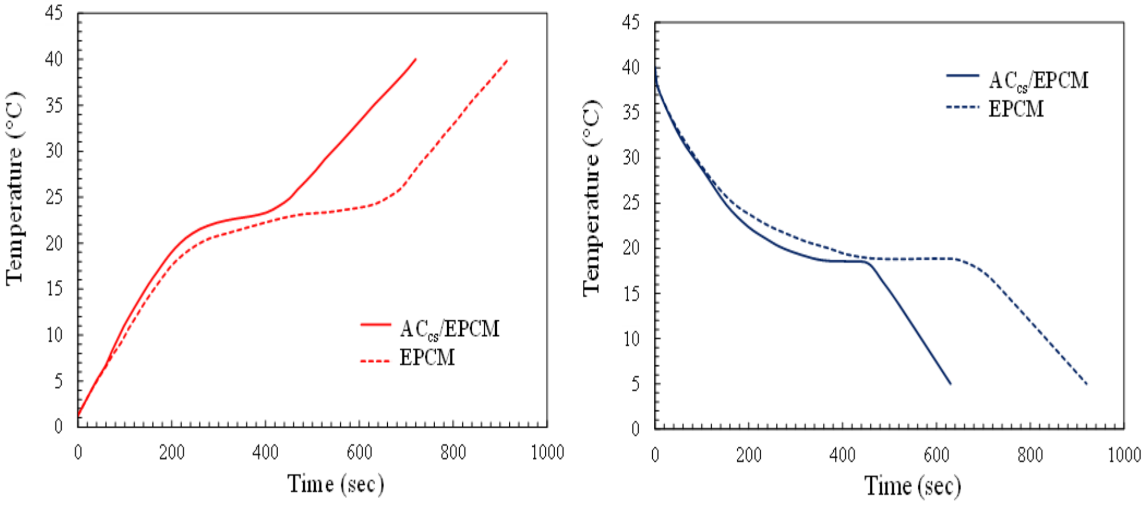

Figure 3.13: T-history analysis (a) melting; (b) crystallization

3.6 Mechanical performance

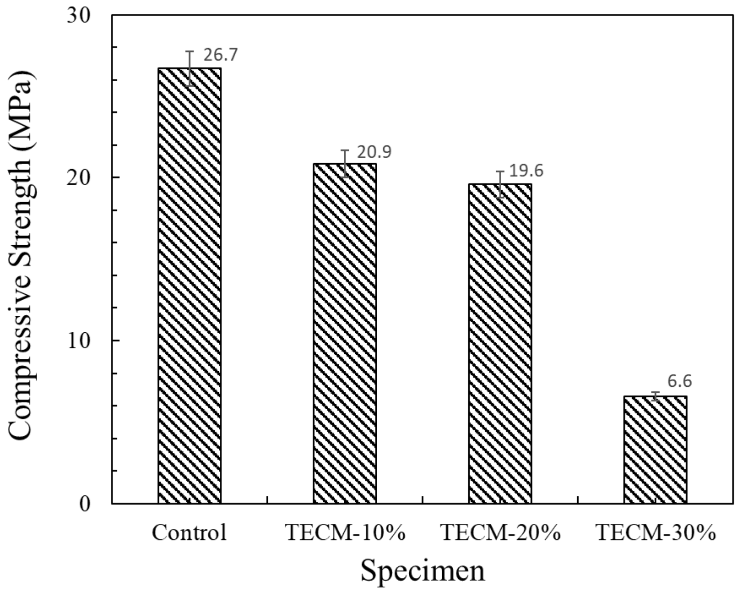

Figure 3.14: Compressive strength after 28 days of the control and TESCM samples

Compressive strength tests were conducted on both control and TECM samples after 28 days of curing. For each type of sample, three specimens were tested to failure to determine their compressive strength. The average values of compressive strengths along with their corresponding standard deviations are presented in Fig. 3.14 providing insights into the mechanical performance of cement mortar. The control sample exhibited a relatively high compressive strength; i.e., 26.7 MPa at 28 days. However, a noticeable reduction in compressive strength was observed in the samples containing AC_{cs}/EPCM composite. Specifically, as the proportion of composite PCM increased the compressive strength of TECMs decreased significantly as reported in the literature [13,14]. At 28-days, the compressive strengths of the TECM-10%, TECM-20% and TECM-30% samples were 21.7%, 26.6% and 75.3% lower than that of the control sample, respectively. This sharp decline in strength is attributed to the porous structure of AC_{cs} which reduces the overall density and strength of cement mortar.

3.7 Thermal conductivity of TECM

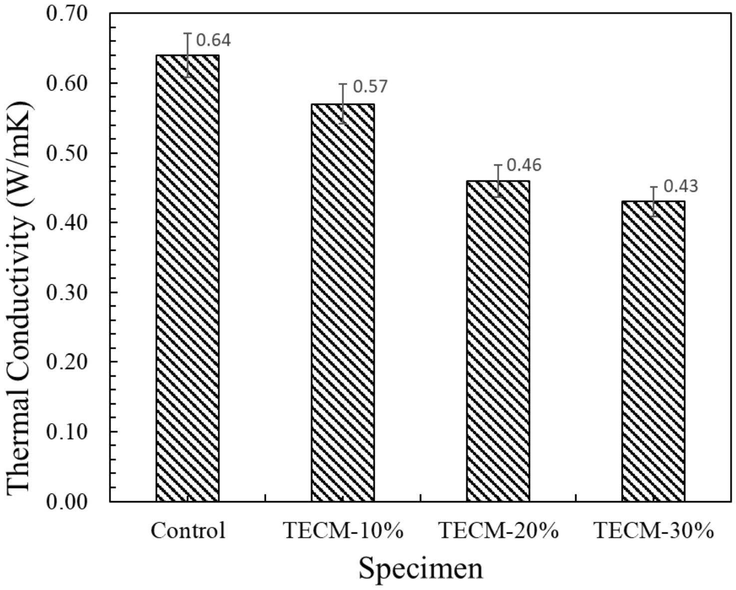

Figure 3.15: Thermal conductivity of mortar samples with/without AC_{cs}/EPCM

Figure 3.15 presents the test results for investigated specimens showing a consistent decline in thermal conductivity with an increasing substitution ratio of the AC_{cs}/EPCM composite. Specifically, the thermal conductivity values for the control sample, TECM-10%, TECM-20% and TECM-30% were recorded at 0.64, 0.57, 0.46 and 0.43 $W{\cdot}m^{-1}{\cdot}K^{-1}$, respectively. In addition, there was a reduction of 12%, 39% and 49% reduction in thermal conductivity as compared to the control sample. This behavior is consistent with the past research, e.g., [15,16]. The possible cause for this reduction can be attributed to the inherently low thermal conductivity of fatty acids (typically ranges 0.16–0.20 W/mK) [10] in comparison with the substituted mineral component; i.e., natural sand has an average thermal conductivity between 1.80–2.50 W/mK [17–19]. Moreover, the volume of entrapped air during the inclusion of composite PCM leads to higher porosity which is also a prominent factor for reduced thermal conductivity [20].

3.8 Thermoregulation performance

In the initial cooling phase, the inner surface temperature of the control mortar drops rapidly from approximately 20°C to 14.4°C while the TECM-30% demonstrated a more gradual decrease stabilizing around 16.6 °C indicating a thermal delay due to latent heat absorption. Similarly, the outer surface temperature of the control mortar panel drops sharply from 20°C to nearly 11.6 °C whereas the TECM-30% maintains a slightly higher temperature around 17.5°C showing improved heat retention. During the heating phase, the control mortar reached its peak temperature rapidly at 32.5°C whereas the TECM-30% mortar panel exhibited a less rapid increase than the control and delayed the peak temperature. Thus, TECM-30% performed better than control mortar showing fewer thermal fluctuations indicating an efficient integration of AC_{cs}/EPCM composite for improved building energy efficiency.

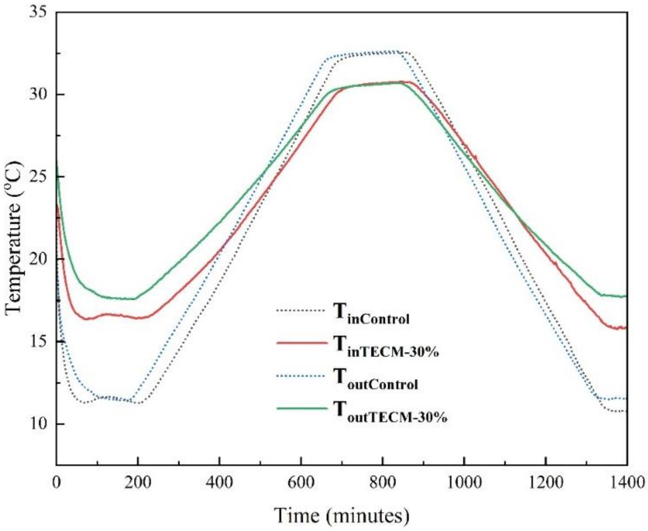

Figure 3.16: Thermoregulation performance demonstration through temperature fluctuations

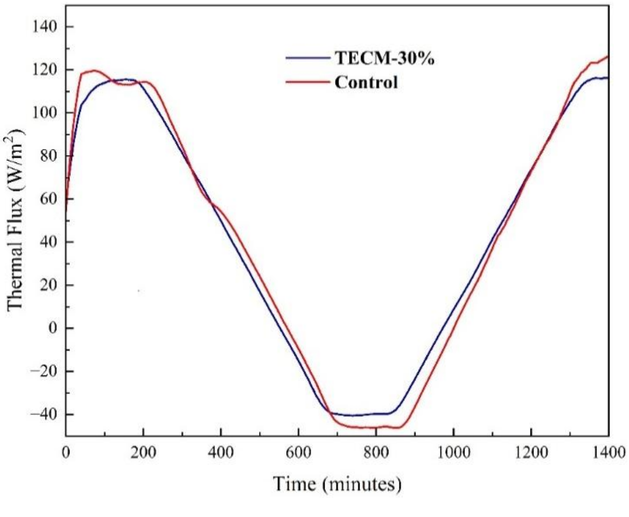

Figure 3.17: Thermoregulation performance demonstration through thermal flux

4 Discussion

The integration of biobased PCM with activated carbon derived from waste coconut shells represents an innovative approach to enhancing TES characteristics in construction materials. This study explores the synergistic combination of CA-MA-based EPCM with AC_{cs} forming a stable and leak-proof composite material. The composite was subsequently incorporated into cement-based mortar (TECMs) in different proportions to assess its potential for improving thermal performance in buildings. The fundamental objective of this thesis is to enhance energy efficiency and promote sustainable building practices by utilizing agricultural waste materials.

One of the key advantages of using AC_{cs} as a PCM carrier is its high porosity and large surface area which facilitate superior heat transfer and storage. The experimental findings demonstrated that the impregnation of EPCM into AC_{cs} resulted in a well-dispersed composite with stable thermal properties. DRIFT-FTIR analysis confirmed that there was no significant chemical reaction between AC_{cs} and EPCM indicating that the composite's integrity was maintained. Additionally, DSC analysis revealed that the AC_{cs}/EPCM composite exhibited a latent heat storage capacity of 32.5 J/g with a melting temperature of approximately 21.8 °C. These properties make it an effective candidate for passive thermal regulation in buildings where it can absorb excess heat during the daytime and release it at night reducing reliance on active cooling and heating systems.

Thermal degradation analysis conducted using thermogravimetry further confirmed the thermal stability of the AC_{cs}/EPCM composite up to 155°C. SEM images provided valuable insights into the morphology of the composite highlighting a uniform dispersion of PCM within the porous AC_{cs} framework. This uniformity ensures consistent thermal performance and minimizes the risk of leakage during phase transitions. Moreover, the composite was tested under accelerated thermal cycling conditions and demonstrated excellent thermal reliability. The composite retained its phase change characteristics even after 1000 cycles and the latent heat storage capacity also remained largely unaffected. These results indicate that AC_{cs} can act as an excellent support material for biobased PCM enhancing its efficiency and prolonged serviceability in TES applications.

The addition of AC_{cs} improved the thermal conductivity of the composite PCM from 0.17 $W/m\cdot K^{-1}$ to 0.30 $W/m\cdot K^{-1}$ marking a 43% enhancement. This increase is attributed to the high surface area of AC_{cs}, its interconnected porous structure and the presence of carbonized material which facilitates heat transport more efficiently than pure EPCM. In addition to improved thermal conductivity, the T-history method was utilized to evaluate the thermal response and heat storage efficiency of the AC_{cs}/EPCM composite. The results revealed that the AC_{cs}/EPCM composite exhibited a significant reduction in both melting and solidification times compared to pure EPCM. The composite PCM melted in approximately 417 sec compared to 648 sec for pure EPCM demonstrating a 35% improvement in heating efficiency. Similarly, the solidification time is reduced by 30%, from 651 sec to 454 sec indicating faster heat release capabilities. These findings confirm that the incorporation of AC_{cs} not only enhances thermal conductivity but also accelerates the overall heat transfer process making the composite PCM a more efficient material for TES applications.

Despite the numerous thermal advantages, incorporating AC_{cs}/EPCM into TECMs significantly influenced the physical and mechanical characteristics. The water absorption increased with higher composite PCM content due to increased porosity which can be advantageous for improving thermal insulation properties albeit with a reduction in mechanical characteristics. The compressive strength of TECM samples decreased as the proportion of AC_{cs}/EPCM increased with the value dropping from 26.7 MPa for the control sample to 20.9 MPa, 19.6 MPa and 6.6 MPa for TECM-10%, TECM-20% and TECM-30%, respectively. While this decline in strength may limit its application in load-bearing structures, this remains highly suitable for non-structural components such as wall panels, insulation layers and interior coatings. The reduced density of TECM samples varied between 875 kg/m^3 and 1129 kg/m^3 categorizing it as a lightweight material making it beneficial for energy-efficient construction. Moreover, the thermal conductivity values for the control sample, TECM-10%, TECM-20% and

TECM-30% were measured at 0.64, 0.57, 0.46, and 0.43 $W \cdot m^{-1} \cdot K^{-1}$, respectively. This represents a reduction in thermal conductivity of 12%, 39%, and 49% for TECM-10%, TECM-20%, and TECM-30%, respectively compared to the control sample. It can be concluded that the inclusion of composite PCM enhances the material's microstructure potentially increasing porosity which further impedes heat flow.

The thermoregulation performance of AC_{cs}/EPCM incorporated cement mortar demonstrated a substantial improvement in thermal management compared to conventional control mortar. During the initial cooling phase, TECM-30% exhibited a more gradual decrease in surface temperature stabilizing around 16.6°C for the inner surface and 17.5°C for the outer surface as opposed to the rapid drop observed in the control mortar. This delayed thermal response is indicative of the PCM’s latent heat absorption which mitigates rapid temperature fluctuations and improves thermal buffering. Similarly, during the heating phase, TECM-30% showed a delayed peak temperature with lower inner and outer surface temperatures (30.5°C and 30.8°C, respectively) compared to the control mortar (32.5°C) further confirming the PCM’s heat retention capabilities. The reduction in thermal flux observed in TECM-30% throughout the test cycle reflected its enhanced ability to moderate heat transfer. The enhanced thermal buffering demonstrated in thermoregulation assessment alongside the PCM's ability to store and release thermal energy highlights the potential of thermally enhanced cement mortar with composite PCM for improving building energy efficiency and maintaining more stable internal temperatures for effective thermoregulation performance.

From a technical perspective, the use of AC_{cs}/EPCM composite aligns with the global shift towards sustainable and energy-efficient building materials. The utilization of agricultural waste such as waste coconut shells contributes to a circular economy by repurposing biomass into high-value TES materials. The activated carbon derived from these shells enhances the thermal conductivity of PCM while offering an eco-friendly alternative to conventional carriers relying on natural resources such as bentonite, diatomite and natural clay among others. The vacuum-assisted impregnation process used in this study ensures deep penetration of PCM into the porous structure of AC_{cs} minimizing leakage and enhancing cycling stability. These characteristics make AC_{cs}/EPCM composite an attractive option for innovative thermal management solutions in the construction industry. Given these improvements, the AC_{cs}/EPCM composite shows great potential for use in building envelopes and other energy-efficient thermal management systems. The integration of such composite into construction materials, such as concrete, wallboards, and insulation panels could enhance indoor thermal comfort while reducing heating and cooling energy demands. This is particularly beneficial in regions with extreme temperature variations where passive temperature regulation can significantly lower energy consumption.

Future research could focus on optimizing the mechanical properties of TECM composite to expand their applicability to structural components. One approach could involve reinforcing the mortar with nano-additives or hybrid fillers that enhance both mechanical strength and thermal storage capacity. Additionally, further investigation could focus on assessing the long-term durability of these composite in diverse climatic conditions considering factors such as humidity resistance, thermal fatigue, and phase stability over extended periods. Furthermore, integrating TES materials with smart building technologies such as adaptive climate control systems and dynamic facades could further enhance their energy efficiency and contribute to the development of net-zero energy buildings.

4.1 Field implication

The integration of AC_{cs} with EPCM as a composite PCM presents a significant advancement in improving the thermal inertia and service life of cement-based construction materials [21]. Traditional PCMs when directly added to cement interfere with the hydration process necessary for the formation of calcium silicate hydrates (C-S-H) which are crucial for the mechanical strength of cementitious materials [22,23]. However, encapsulating the PCM within a material e.g., AC_{cs} circumvents this problem as the porous structure of AC_{cs} not only confines the PCM but also prevents leakage and preserves the integrity of the cementitious matrix. Furthermore, the high thermal conductivity of AC_{cs} enhances heat transfer within the composite material improving its overall thermal performance. Moreover, EPCM with a suitable melting temperature and appropriate phase change enthalpy of the corresponding composite material favors their utilization in TES applications especially in buildings where it can help regulate indoor temperatures to maintain thermal comfort. This reduces the reliance on heating, ventilation and air conditioning (HVAC) systems leading to significant energy savings [24]. Moreover, AC_{cs} is an environmentally friendly material offering a sustainable way to repurpose agricultural waste which helps mitigate pollution from discarded coconut shells. The dual benefit of thermal management and waste recycling enhances the environmental and economic value of the AC_{cs}/EPCM composite.

The developed composite material-based cementitious materials can be utilized to construct various building elements like walls, roofs, ceilings and floors where its ability to absorb and release heat is optimized efficiently [25,26]. Thus, AC_{cs} promotes the building application of the PCM making it a promising choice for the construction industry. By embedding AC_{cs}/EPCM composite into these building components, excess heat absorbed from solar radiation can be stored and later released. Consequently, temperature fluctuations can be managed inside buildings and easing the load on HVAC systems. This contributes to energy-efficient and sustainable building designs. For practical applications, AC_{cs}/EPCM composite must exhibit appropriate mechanical properties to withstand the stresses of construction and use. It also needs to maintain cycling stability over an extended period to ensure long-term performance [27]. In addition, the thermoregulation performance of composite needs to be evaluated under varying seasonal conditions to validate its reliable performance throughout the year. The development of AC_{cs}/EPCM composite holds great potential for modern construction offering a pathway to energy-efficient building materials that also address environmental concerns. Future research could focus on the evaluation of the mechanical and thermal characteristics of the AC_{cs}/EPCM composite with cementitious material.

5 Conclusions

This study has explored an innovative approach to TES in construction materials focusing on the integration of biobased PCM with activated carbon derived from waste coconut shells. The work presented in this thesis has aimed to advance the development of sustainable and energy-efficient building materials capable of improving the thermal performance of buildings while contributing to environmental sustainability.

- The integration of biobased PCM with activated carbon derived from agricultural waste (coconut shells) presents a novel method for enhancing thermal performance in construction materials offering a sustainable solution for passive thermal regulation in buildings.

- The composite material formulated by impregnating EPCM into AC$_{cs}$ demonstrated improved heat storage and transfer capabilities making it suitable for use in buildings. The AC$_{cs}$/EPCM composite exhibited high thermal stability maintaining its phase change characteristics after numerous thermal cycles. This long-term reliability makes it a suitable candidate for TES applications with sustained performance over time.
- The incorporation of AC$_{cs}$ into the composite material enhanced its thermal conductivity, improving the efficiency of heat transfer. This results in more effective thermal management reducing the need for active cooling and heating systems in buildings. AC$_{cs}$/EPCM composite demonstrated faster melting and solidification times compared to pure EPCM, indicating improved heating and cooling efficiency. This reduced time for phase transitions enhances the overall thermal management performance.
- The addition of AC$_{cs}$/EPCM to cement-based mortar (TECM) improved thermal performance. On the other hand, a slight reduction in mechanical characteristics was observed with the addition of composite PCM in cement mortar, however, it remained suitable for non-load-bearing elements such as insulation layers and interior coatings. The developed thermally enhanced cement mortar demonstrated superior thermal buffering capabilities showing a more gradual temperature change during both heating and cooling phases. This behavior ensures stable internal building temperatures enhancing comfort and energy efficiency.
- Using agricultural waste such as coconut shells for activated carbon production aligns with the principles of a circular economy repurposing biomass into valuable TES material. This sustainable approach reduces the environmental impact of thermal management systems. The AC$_{cs}$/EPCM composite provides a promising solution for improving energy efficiency in buildings. Its incorporation into construction materials such as cement mortar, wall panels and insulation layers could reduce energy consumption by minimizing reliance on active heating and cooling systems.

The performance and stability of the AC$_{cs}$/EPCM composite in laboratory tests indicate its potential for large-scale TES applications in the construction industry. This technology can be integrated into building materials to enhance energy efficiency, contributing to the global push towards sustainable and eco-friendly construction practices. This study highlights the promising potential of utilizing agricultural waste materials, such as coconut shells, for the development of sustainable thermal management solutions. By improving energy efficiency and reducing the environmental impact of conventional building materials, AC$_{cs}$/EPCM composite represents an innovative step forward in the quest for more sustainable construction practices. Meanwhile, it is recommended that future work could focus on enhancing the composite’s strength without compromising its thermal performance as well as investigating its behavior in different environmental conditions.

Súhrn

Táto dizertačná práca skúma vývoj energeticky účinného kompozitného materiálu na skladovanie tepelnej energie integráciou materiálu s fázovou zmenou (PCM) na biologickej báze s aktívnym uhlím získaným z biomasy, konkrétne zo škrupín kokosových orechov. Štúdia sa zameriava na zvýšenie tepelného výkonu kompozitu impregnáciou eutektickej zmesi na biologickej báze kyseliny kaprinovej a kyseliny

myristovej ako PCM do aktívneho uhlíkového materiálu na báze kokosovej škrupiny, čo vedie k nepriepustnému kompozitnému materiálu. Zistili sme, že aktívne uhlie účinne zadržiava významné množstvo PCM tým, že hmota prispieva k vytvoreniu stabilného kompozitu. Na hodnotenie vlastností kompozitu sa použili rôzne charakterizačné techniky vrátane skenovacej elektrónovej mikroskopie, termogravimetrickej analýzy, infračervenej spektroskopie s Fourierovou transformáciou, diferenciálnej skenovacej kalorimetrie a tepelných cyklických testov. Naše výsledky ukázali, že kompozitný PCM vykazoval stabilné teploty fázovej zmeny a významné latentné teplo. Okrem toho kompozitný materiál vykazoval silnú odolnosť voči tepelnej degradácii a vykazoval spoľahlivý výkon počas viacerých tepelných cyklov. Schopnosť kompozitu udržiavať stabilné teploty fázovej zmeny pri poskytovaní vhodného latentného tepla ďalej zdôraznila jeho potenciál pre aplikácie na skladovanie energie. Keď sa kompozitný PCM zapracoval do cementovej malty, pevnosť v tlaku dosahovala vcelku prijateľné hodnoty a preukázalo sa zlepšenie tepelnej regulácie. Maltové panely obsahujúce kompozitný PCM vykazovali zlepšené tepelné oneskorenie a znížené špičkové teploty počas fázových prechodov, čo naznačuje efektívne tepelné riadenie. Tieto zistenia naznačujú, že kompozitný PCM má významný potenciál pre energeticky účinné stavebné materiály, ktoré ponúkajú výhody termoregulácie a vylepšené materiálové vlastnosti pre stavebné aplikácie. Táto štúdia predstavuje potenciál bio-založeného PCM pri presadzovaní udržateľných a energeticky účinných technológií pre stavebný priemysel.

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List of Publications

1. **Junaid, Muhammad Faisal**, Zia ur Rehman, Nauman Ijaz, Rashid Farooq, Usama Khalid, and Zain Ijaz. Performance evaluation of cement-based composites containing phase change materials from energy management and construction standpoints. (**Citations in WoS: 22**)
   Published: Feb 2024 in **Construction and Building Materials**
2. Ijaz, Nauman, Wei-Min Ye, Zia ur Rehman, Zain Ijaz, and **Muhammad Faisal Junaid**. Global insights into micro-macro mechanisms and environmental implications of limestone calcined clay cement (LC3) for sustainable construction applications. (**Citations in WoS: 38**)
   Published: Jan 2024 in **Science of the Total Environment**
3. Khalid, Usama, Zia Ur Rehman, Nauman Ijaz, Inamullah Khan, and **Muhammad Faisal Junaid**. Integrating wheat straw and silica fume as a balanced mechanical ameliorator for expansive soil: a novel agri-industrial waste solution. (**Citations in WoS: 11**)
   Published: Jun 2023 in **Environmental Science and Pollution Research**
4. Ijaz, Nauman, Weimin Ye, Zia ur Rehman, Zain Ijaz, and **Muhammad Faisal Junaid**. New binary paper/wood industry waste blend for solidification/stabilisation of problematic soil subgrade: macro-micro study. (**Citations in WoS: 32**)
   Published: May 2023 in **Road Materials and Pavement Design**
5. Zia ur Rehman, **Muhammad Faisal Junaid**, Nauman Ijaz, Usama Khalid, and Zain Ijaz. Remediation methods of heavy metal contaminated soils from environmental and geotechnical standpoints. (**Citations in WoS: 59**)
   Published: Apr 2023 in **Science of the Total Environment**

6. Čurpek, Jakub, Miroslav Čekon, Ondřej Šikula, and **Muhammad Faisal Junaid**. Challenges in BiPV/PCM Facade System: Pathways Towards Numerical Modelling and Simulation Approaches. (**Citations in WoS: 0**)
   Published: 2023 in **Smart Innovation, Systems and Technologies**
7. **Junaid, Muhammad Faisal**, Zia ur Rehman, Nauman Ijaz, Miroslav Čekon, Jakub Čurpek, and Ahmed Babeker Elhag. Biobased phase change materials from a perspective of recycling, resources conservation and green buildings. (**Citations in WoS: 27**)
   Published: Sep 2022 in **Energy and Buildings**
8. **Junaid, Muhammad Faisal**, Zia ur Rehman, Michal Kuruc, Igor Medveď, Darius Bačinskas, Jakub Čurpek, Miroslav Čekon, Nauman Ijaz, and Wajahat Sammer Ansari. Lightweight concrete from a perspective of sustainable reuse of waste byproducts. (**Citations in WoS: 100**)
   Published: Feb 2022 in **Construction and Building Materials**
9. Ansari, Wajahat Sammer, Jun Chang, Zia ur Rehman, Usman Nawaz, and **Muhammad Faisal Junaid**. A novel approach to improve carbonation resistance of Calcium Sulfoaluminate cement by assimilating fine cement-sand mix. (**Citations in WoS: 19**)
   Published: Jan 2022 in **Construction and Building Materials**
10. **Junaid, Muhammad Faisal**, Zia ur Rehman, Miroslav Čekon, Jakub Čurpek, Rashid Farooq, Hongzhi Cui, and Imran Khan. Inorganic phase change materials in thermal energy storage: A review on perspectives and technological advances in building applications. (**Citations in WoS: 127**)
    Published: Dec 2021 in **Energy and Buildings**