

Pyrolysis temperature controls the accessible pore volume and capric acid encapsulation efficiency of coconut shell biochar

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Abstract

Waste-derived biochar is a low-cost scaffold for shape-stabilized phase change materials (PCMs), yet how pyrolysis temperature governs the pore volume a molten PCM can reach remains unresolved. Here we decouple surface area from pore accessibility by preparing ZnCl_2 -activated coconut shell biochars at 550, 700, 850 and 1000 °C under an identical protocol and impregnating them with capric acid. Contrary to the assumption that higher BET surface area guarantees greater PCM loading, encapsulation efficiency tracks the pore volume accessible on the adsorption branch. Between the 850 and 1000 °C biochars the BET area differs by only 3.3%, whereas the BJH adsorption cumulative pore volume differs by 17.6% (0.1102 versus 0.1296 $\text{cm}^3 \text{g}^{-1}$) and the encapsulation efficiency by 18.5% (57.59 versus 68.25%). High-resolution TEM resolves the origin: short, curved graphene fringes constrict pore entrances at 850 °C, whereas extended parallel stacks bound open channels at 1000 °C. Efficiency rises from 42.25% at 550 °C to 68.25% at 1000 °C; the optimized composite delivers 112.88 J g^{-1} , does not leak at 55 °C and retains 99% of its latent heat after 500 cycles. Accessible pore volume, not surface area, is the key design criterion for biochar PCMs in passive building thermal regulation.

Keywords Biochar-PCM composite · Pyrolysis temperature · Accessible pore volume · Pore neck accessibility · Latent heat storage · Capric acid

Introduction

The thermal management of buildings accounts for nearly one third of global energy use, a figure that continues to rise as urbanization intensifies^{1,2}. Within this context, passive regulation using phase change materials has been repeatedly validated as a low-exergy strategy to shave peak loads and improve occupant comfort^{3,4}. Capric acid, a fatty acid with a melting point near 35 °C, is particularly suitable for building envelopes because it offers high latent heat, negligible supercooling, and long-term chemical stability^{5,6}. However, two persistent limitations have

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hampered its practical deployment: leakage of the liquid phase above the melting point and intrinsically poor thermal conductivity, typically below $0.25 \text{ W m}^{-1} \text{ K}^{-1}$ ^{17,8}. A large body of work has therefore focused on porous supports that confine the molten PCM by capillary forces while simultaneously raising thermal diffusivity^{9,10}.

Among the many support materials explored, carbonaceous matrices are especially attractive because of their high specific surface area, good thermal conductance, and chemical inertness^{11–13}. Their production from fossil or high-purity precursors is, however, energy-intensive and costly, which restricts large-scale use^{14,15}. Biochar, obtained by pyrolyzing biomass under oxygen-limited conditions, has recently emerged as a low-cost, renewable, and carbon-negative alternative^{16–18}. Its hierarchical pore structure, inherited from the lignocellulosic feedstock, can be tuned by varying the pyrolysis temperature, and the partial graphitization that occurs at higher temperatures contributes to thermal transport^{19,20}. Coconut shell, a hard and abundant agricultural residue, yields biochar with a particularly robust carbon framework that withstands high-temperature treatment without excessive collapse^{21,22}.

Biochar–PCM composites have developed rapidly, and Table 7 compiles fifty-six systems reported to date across a wide range of feedstocks and PCMs. Encapsulation efficiencies span 22.6 to 78.8%, with most unmodified supports clustered between 30 and 65%. Three shortcomings recur throughout this body of work. First, the great majority of studies characterize a single pyrolysis temperature, or at most two, so that the relationship between temperature, texture and performance is inferred rather than measured. Second, support quality is almost always reported as BET surface area and total pore volume, metrics that describe how much internal surface exists but not whether a molten PCM can reach it. Third, composite performance is usually reported only as melting enthalpy, without reconciling it against the pore volume that is actually accessible; overestimating the capacity of a support produces composites that lose latent heat on cycling or leak after a few melt–freeze events. The present work addresses all three: a complete 550–1000 °C series is prepared under a single unchanged activation and impregnation protocol, the adsorption-branch pore volume rather than the BET area is identified as the predictive metric and validated against two independent measurements of PCM loading, and the pore-wall architecture responsible for the difference is visualized directly by high-resolution electron microscopy.

The data reported here, obtained from coconut shell biochars pyrolyzed at 550, 700, 850 and 1000 °C and then impregnated with capric acid, reveal a non-monotonic behavior that defies the simple “higher area, higher efficiency” expectation. The sample pyrolyzed at 850 °C exhibits a BET surface area nearly as high as that of the 1000 °C sample, yet its thermal storage efficiency is markedly lower. Meanwhile, the 1000 °C sample, with only a modest increase in area, gives the highest efficiency. This pattern is not an anomaly; it is a window into the evolution of pore accessibility. We demonstrate that at 850 °C the biochar develops a significant fraction of ink-bottle or constricted pores, which contribute to the BET area but are not fully infiltrated by molten capric acid. At 1000 °C, further thermal etching widens the pore entrances, converting the same or even a slightly larger pore volume into an accessible network. If this hypothesis is correct, then total pore volume and BET area are insufficient predictors; what matters is the *adsorption branch* of the isotherm and, more practically, the PCM-accessible pore volume measured by a technique such as BJH on the adsorption leg.

This behaviour is at odds with the way the relationship between pyrolysis temperature and the effectiveness of biochar as a PCM support is usually presented, namely as monotonic: higher temperature gives higher surface area, which in turn should give higher PCM loading and higher thermal efficiency^{23,24}. This linear picture, however, ignores the distinction between total pore volume and *accessible* pore volume. Chemical activation studies have shown that a large BET surface area does not guarantee that a liquid PCM can enter the pore network, especially when pore necks become constricted or when the pore system develops an ink-bottle morphology^{25,26}. Conversely, a highly microporous structure can immobilize PCM molecules but also restrict their crystallization, leading to a significant loss of latent heat^{27,28}.

The pyrolysis temperature exerts contradictory effects on biochar texture. At low to moderate temperatures (500–700 °C), the release of volatiles gradually creates micropores and mesopores, increasing both surface area and pore volume^{29,30}. As the temperature rises beyond 800 °C, further carbonization can cause pore coalescence,

but it may also induce the formation of narrow pore entrances while preserving a larger internal cavity, i.e. an ink-bottle geometry^{31,32}. Such a structure is fully accounted for by BET analysis, but it is poorly accessible to a viscous or waxy PCM melt.

We therefore present a comprehensive analysis of four biochars, correlating their BET surface area, total pore volume, low-pressure N₂ uptake, and BJH adsorption pore volume with the phase change enthalpy, encapsulation efficiency, and thermal reliability of the corresponding capric acid composites. Our results demonstrate that accessible pore volume, not total surface area, governs the thermal storage performance. They also show that the 1000 °C biochar achieves an encapsulation efficiency of 68% of the pure capric acid value, which is among the highest reported for an unmodified waste-derived biochar^{33,34}. By exposing the hidden role of pore neck widening, this study provides a design rule: for coconut shell and similar hard lignocellulosic feedstocks, the optimal pyrolysis temperature for PCM support lies at the upper end of the investigated range, because only there does the pore network become fully accessible. The findings also raise a cautionary note about interpreting BET data in isolation, a practice that remains regrettably common in the PCM literature^{35,36}. Finally, the use of a waste biomass that would otherwise be burned or landfilled, together with the carbon-negative nature of biochar, aligns this work with circular economy and carbon neutrality objectives; the associated carbon balance is quantified in section “[Sustainability assessment](#)”.

Materials and methods

Materials

Capric acid (CA, purity ≥ 98%) was purchased from Daejung Chemicals, Republic of Korea, and used as received without further purification. Coconut shells were collected from a local market in Chandrakona Town, West Bengal, India. The shells were manually crushed and sieved to retain the 5–10 mm size fraction, washed repeatedly with distilled water to remove surface impurities, and dried in an electric oven at 105 °C for 24 h. Zinc chloride (ZnCl₂, analytical grade) was obtained from Duksan Chemical Reagent, Republic of Korea. All other chemicals were of analytical grade.

Preparation of ZnCl₂-activated coconut shell biochars

The dried coconut shell pieces were chemically activated by impregnation with a 1.27 mol L⁻¹ ZnCl₂ aqueous solution (173.1 g L⁻¹) at a solid-to-liquid ratio of 1:2 (w/v) for 12 h at room temperature. These conditions correspond to an impregnation ratio of 0.35 g ZnCl₂ per g of dry precursor, which lies within the 0.3–0.5 range generally reported as optimal for the ZnCl₂ activation of hard lignocellulosic feedstocks: lower ratios leave the dehydration and aromatization reactions incomplete and yield a predominantly microporous char, whereas higher ratios cause excessive pore widening, loss of micropore walls and a marked reduction in yield. The 1:2 (w/v) ratio is the minimum liquid volume required to submerge and wet the dense shell pieces completely. The activation conditions were held identical for all four batches so that peak pyrolysis temperature remained the only experimental variable in this study. After impregnation, the mixture was dried at 105 °C for 12 h.

Pyrolysis was carried out in an electric muffle furnace (Model MSF-22, Lab House, Republic of Korea) under a limited oxygen atmosphere. Before each run, the furnace chamber was flushed with high-purity nitrogen gas (99.999%) for 5 min to displace air. Approximately 300 g of the dried ZnCl₂-impregnated material was placed in a ceramic crucible and heated from room temperature to the target temperature at a rate of 10 °C min⁻¹. Four peak pyrolysis temperatures were investigated: 550 °C, 700 °C, 850 °C and 1000 °C. The sample was held at the target temperature for 1 h and then allowed to cool naturally to room temperature. The resulting biochars were washed with 0.1 mol L⁻¹ hydrochloric acid and then with distilled water until the pH of the filtrate reached 6.5–7.0. The acid wash serves three purposes. It dissolves the residual activating agent together with the ZnO,

Zn(OH)₂ and zinc oxychloride phases formed during pyrolysis, which are insoluble in water but readily soluble in dilute hydrochloric acid; it thereby liberates the pore volume that the zinc salt had occupied within the carbon framework, so that the wash forms part of the pore-generating process rather than being merely a cleaning step; and it eliminates zinc species that could otherwise catalyze degradation or esterification of the capric acid during prolonged thermal cycling, along with soluble alkali and alkaline-earth ash constituents. A concentration of 0.1 mol L⁻¹ was chosen as sufficient to dissolve the zinc phases without oxidative attack on the carbon framework, and washing was continued to near-neutral pH so that no residual acidity remained. Finally, the products were dried at 105 °C for 12 h, ground and sieved to a particle size below 150 µm before impregnation with capric acid, and stored in airtight vials. The mass of each batch was recorded before impregnation and again after acid washing and final drying. The biochar yield is expressed as the mass of washed and dried biochar per unit mass of dried ZnCl₂-impregnated precursor and is reported in Table 1. The samples were designated as CSB 5.5, CSB 7.0, CSB 8.5 and CSB 10 according to their pyrolysis temperature.

Preparation of capric acid/biochar shape-stabilized PCM composites

The shape-stabilized phase change material (SSPCM) composites were prepared by vacuum impregnation. For each composite, a pre-calculated amount of capric acid was melted in a glass beaker at 50 °C. The corresponding biochar (CSB 5.5, CSB 7.0, CSB 8.5 or CSB 10) was added to the molten CA at a biochar-to-CA mass ratio of 1:3. The mixture was stirred at 800 rpm for 15 min to ensure preliminary dispersion. The beaker was then transferred into a vacuum drying oven and subjected to a vacuum of −0.1 MPa (gauge) at 50 °C for 3 h. Following impregnation, excess CA on the biochar surface was first removed using filter paper, and the composite was then placed on filter paper in a vacuum oven for further removal of residual CA. The resulting SSPCM composites were denoted as CBC 5.5, CBC 7.0, CBC 8.5 and CBC 10, where CBC stands for coconut shell biochar-capric acid. A schematic illustration of the overall synthesis procedure, from raw coconut shells to the final shape-stabilized PCM composites, is presented in Fig. 1.

Characterization

Scanning electron microscopy and energy dispersive X-ray spectroscopy

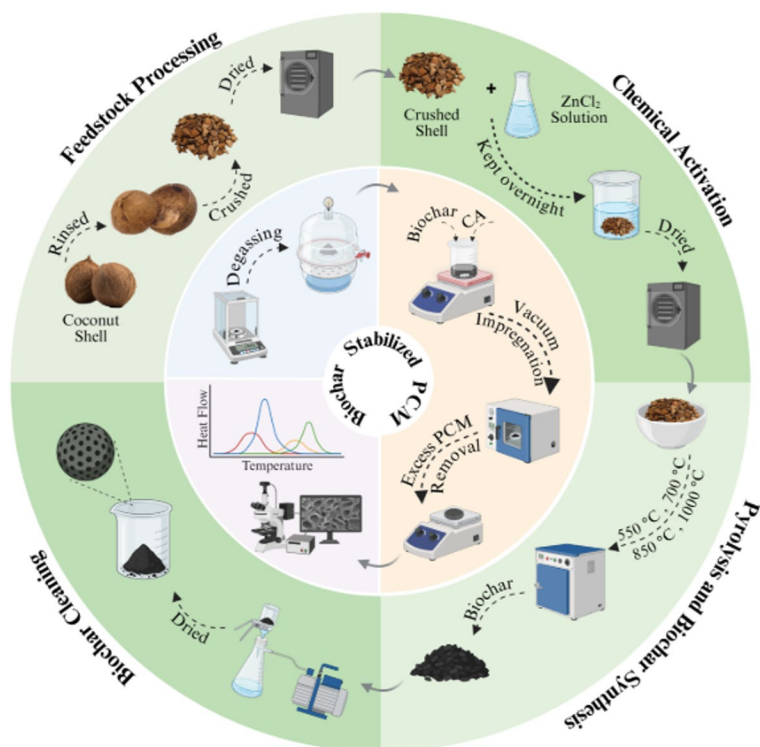
The surface morphology of the biochars and the SSPCM composites was examined using a field emission scanning electron microscope (FE-SEM, SU5000, Hitachi, Japan) operated at an accelerating voltage of 15 kV. Samples were mounted on aluminum stubs using conductive carbon tape and sputter-coated with platinum to enhance conductivity. Energy dispersive X-ray spectroscopy (EDS) was performed with the same instrument to determine the elemental composition of the biochar surfaces. For the analysis reported here the four biochars were examined by area mapping on an independent energy-dispersive spectrometer (Bruker, 15 kV, 2000× magnification) with an element list comprising carbon, nitrogen, oxygen, silicon, phosphorus and sulfur, and the quantification is

Table 1 Biochar yield and surface elemental composition of the ZnCl₂-activated coconut shell biochars.

Sample	Pyrolysis temp. (°C)	Yield (mass%)	Elemental composition* (mass%)					
			C	N	O	P	S	Si
CSB 5.5	550	40.6	65.96±23.71	15.89±9.69	15.73±7.87	2.23±0.36	0.18±0.11	0.01±0.01
CSB 7.0	700	34.2	67.54±24.46	15.77±9.98	14.11±7.42	2.23±0.36	0.28±0.13	0.08±0.10
CSB 8.5	850	27.6	73.01±24.51	20.53±10.11	4.98±2.82	1.32±0.24	0.13±0.10	0.02±0.01
CSB 10	1000	23.7	74.18±25.39	20.75±11.02	3.52±2.41	1.43±0.26	0.07±0.09	0.04±0.01

* Values were obtained by EDS area mapping (Bruker, 15 kV, 2000×) with an element list comprising C, N, O, Si, P and S, and are quoted with the 3σ absolute errors returned by the instrument. Energy-dispersive spectroscopy cannot quantify light elements in a carbon-dominated matrix (section “[Scanning electron microscopy and energy dispersive X-ray spectroscopy](#)”); these values establish which elements are present and the direction in which each changes with pyrolysis temperature, not their absolute abundances.

Fig. 1 Schematic of the synthesis procedure (biochar preparation and vacuum impregnation of capric acid).



reported in Table 1 together with the 3σ absolute errors returned by the instrument. It should be stated at the outset that energy-dispersive spectroscopy cannot quantify light elements in a carbon-dominated matrix. The photon budget below approximately 0.6 keV is apportioned among carbon, nitrogen and oxygen by a deconvolution that is under-determined at these energies, so that the composition returned depends on the element list supplied to the fitting routine. The compositions reported in this work are therefore to be read as establishing which elements are present and the direction in which each changes with pyrolysis temperature, and no absolute light-element value obtained by this technique is treated as quantitative.

Fourier transform infrared spectroscopy

The chemical functional groups of the biochars and the SSPCM composites were analyzed using a Fourier transform infrared spectrometer (UATR Two, PerkinElmer, Shelton, CT, USA) equipped with an attenuated total reflectance (ATR) accessory. Spectra were recorded in the wavenumber range of 4000 cm^{-1} to 400 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans per sample. A background spectrum was collected before each measurement and automatically subtracted.

BET surface area and pore structure analysis

Nitrogen adsorption-desorption isotherms were measured at 77 K using a surface area and pore size analyzer (ASAP 2460, Micromeritics, Norcross, GA, USA). Prior to analysis, all samples were degassed at 200 °C for 8 h under vacuum to remove adsorbed moisture and gases. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method over a relative pressure (P/P_0) range of 0–1. The total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of $P/P_0 = 0.990$. The pore size distribution was evaluated using the Barrett-Joyner-Halenda (BJH) method applied to the adsorption branch of the isotherm, and the micropore volume was determined using the MP (Mikhail-Brunauer-Bodor) method.

X-ray diffraction

The crystalline structure of the biochar powders was analyzed using an X-ray diffractometer (RINT2000, Rigaku, Japan) equipped with Cu K α radiation ($\lambda = 0.15418$ nm). The instrument was operated at 40 kV and 100 mA. XRD patterns were recorded over the 2θ range of 5° to 70° with a step size of 0.02° and a scanning speed of 6° min^{-1} . Phase identification was carried out by comparison with the International Centre for Diffraction Data (ICDD) database.

Transmission electron microscopy

High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were performed on a JEOL (JEM2100F) transmission electron microscope operated at an accelerating voltage of 200 kV. The biochar powders were dispersed in ethanol by ultrasonication for 15 min and drop-cast onto lacey carbon-coated copper grids, which were dried under vacuum before imaging. Images were recorded digitally at magnifications between $50,000\times$ and $800,000\times$. Lattice-fringe parameters were obtained from the calibrated images by two-dimensional fast Fourier transform, the (002) interlayer spacing being taken from the radial position of the corresponding maximum and the stacking coherence length L_c from its radial width³⁷.

Differential scanning calorimetry and thermogravimetric analysis

The phase change properties of pure capric acid and the SSPCM composites were characterized using a differential scanning calorimeter (DSC Q20, TA Instruments, DE, USA). Samples of 9–10 mg were sealed in standard aluminum pans and heated from 5°C to 50°C at a rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere (flow rate 50 mL min^{-1}), followed by cooling to 5°C at the same rate. The melting temperature (T_m), crystallization temperature (T_s), enthalpy of fusion (ΔH_m) and enthalpy of crystallization (ΔH_s) were recorded. The instrument was calibrated for temperature and enthalpy using indium standard. For thermal cycling stability, the CBC 10 sample was subjected to 500 consecutive heating-cooling cycles using the same DSC program.

Thermogravimetric analysis (TGA) was performed on a thermal analyzer (STA 9, PerkinElmer, USA) under a nitrogen flow of 20 mL min^{-1} . Samples of approximately 10 mg were heated from 30°C to 500°C at a heating rate of $10^\circ\text{C min}^{-1}$. Alumina crucibles were used, and the weight loss curves were recorded.

Leakage resistance, infrared thermal imaging and dynamic thermal response

Leakage resistance and dynamic thermal response were evaluated using the same experimental setup. Approximately 0.5 g of each sample (pure CA, CBC 5.5, CBC 7.0, CBC 8.5 and CBC 10) was placed separately onto Whatman No. 1 filter paper. The filter papers with the samples were placed on a hot plate adjusted to room temperature (25°C) and then heated to 55°C , which is approximately 20°C above the melting point of CA. The samples were maintained at 55°C for 1 h, followed by natural cooling to room temperature over 1 h. For leakage assessment, any soaking or staining on the filter paper was visually inspected to confirm the presence or absence of PCM leakage. Pure CA served as the reference.

For dynamic thermal response, an infrared thermal imaging camera (T250, Teledyne FLIR LLC, USA) was positioned above the same setup. Thermal images were recorded every 10 min during both heating and cooling. The emissivity of the sample surface was set to 0.95. Surface temperatures were extracted from the geometric centre of each sample using the manufacturer's software, and temperature-time profiles were plotted. Only pure CA and the optimized composite CBC 10 are presented for IR thermal imaging and dynamic thermal response.

Results and discussion

Morphology and elemental composition of biochars

The surface morphology of the ZnCl_2 -activated coconut shell biochars pyrolyzed at 550 °C, 700 °C, 850 °C and 1000 °C was examined by scanning electron microscopy. Figure 2 presents the SEM images of CSB 5.5, CSB 7.0, CSB 8.5 and CSB 10 at a magnification of 500 $\times$. At this magnification the images resolve the macroscopic cellular framework inherited from the coconut shell, that is the vessel and gas pores of the original lignocellulosic tissue, together with the roughness of the external particle surfaces. They do not resolve mesoporosity, and no inference about nanometre-scale pore geometry is drawn from them. At the lowest pyrolysis temperature (CSB 5.5, Fig. 2a), the biochar surface appears relatively smooth with occasional shallow depressions. The original cellular structure of the coconut shell is still partially discernible, indicating incomplete thermal decomposition of the lignocellulosic matrix³⁸. Some isolated pores are visible, but their distribution is sparse and the pore walls remain thick.

As the pyrolysis temperature increases to 700 °C (CSB 7.0, Fig. 2b), a pronounced transformation occurs. The surface becomes markedly rougher, and a well-developed porous network emerges. Numerous pores of varying sizes, predominantly in the micrometer range, are visible across the surface. The pore walls appear thinner compared to CSB 5.5, suggesting more extensive volatilization of organic matter and the beginning of carbon framework condensation^{39,40}. This structure is typical of chemically activated biochars where ZnCl_2 promotes dehydration and aromatization reactions^{9,26}.

At 850 °C (CSB 8.5, Fig. 2c), the porous architecture becomes even more complex. The surface exhibits a hierarchical arrangement with both large cavities and abundant smaller pores dispersed on the pore walls.

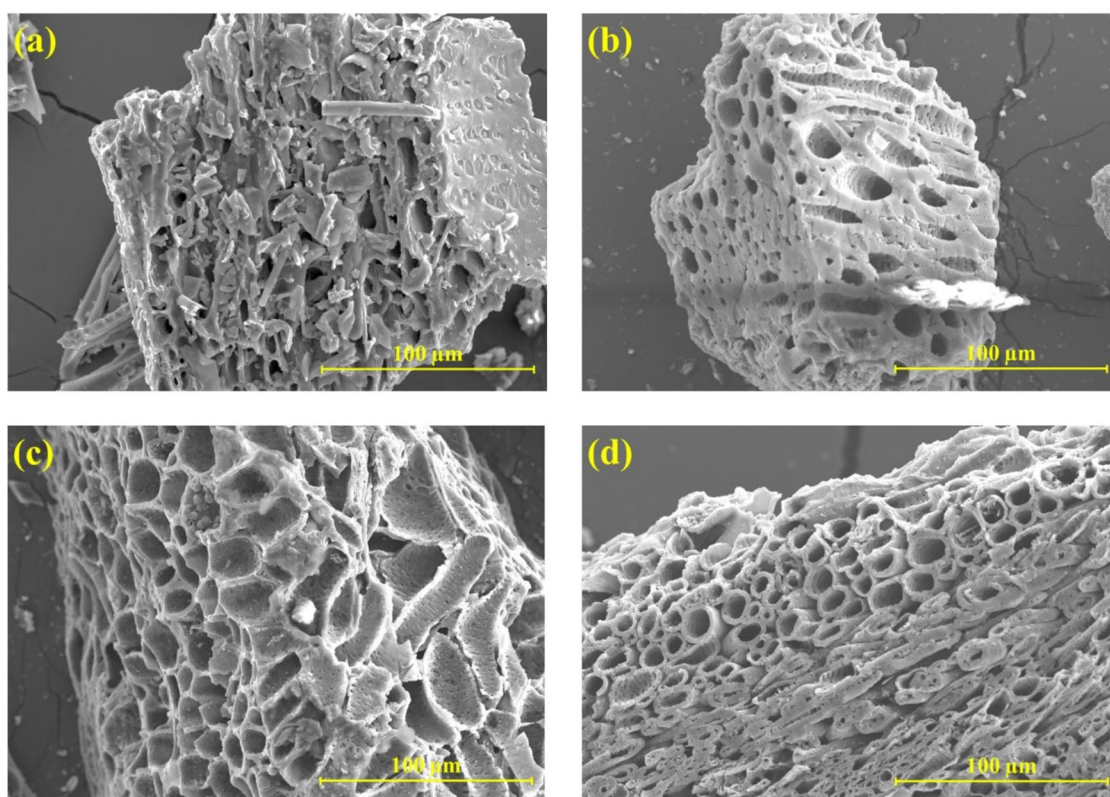


Fig. 2 FESEM images of ZnCl_2 -activated coconut shell biochars pyrolyzed at different temperatures: (a) CSB 5.5 (550 °C), (b) CSB 7.0 (700 °C), (c) CSB 8.5 (850 °C), (d) CSB 10 (1000 °C).

The geometry of the pore entrances, which is the central concern of this work, lies far below the resolution of these images and is examined by nitrogen sorption in section “[Pore structure evolution with pyrolysis temperature](#)” and by high-resolution electron microscopy in section “[Nanoscale pore-wall architecture by HRTEM and SAED](#)”, where the mechanisms proposed for narrowing of the pore entrances during high-temperature pyrolysis are considered^{25,38}.

Further raising the temperature to 1000 °C (CSB 10, Fig. 2d) results in a distinctly different morphology. The pore structure becomes more regular and open. The cell walls appear thinner and the cavity network more regular and better interconnected. The carbon framework appears more rigid and graphitic, which is consistent with the expected increase in carbon ordering at elevated temperatures^{26,38}. Taken together, these observations document a progressive opening and thinning of the macroscopic framework with pyrolysis temperature, which parallels the rise in BET surface area from 481.98 to 758.73 m² g^{−1} reported in section “[Pore structure evolution with pyrolysis temperature](#)” and facilitates transport of the molten PCM to the interior of the particles. They do not, however, address the pore-neck hypothesis of this work, which concerns features one to two orders of magnitude smaller than the resolution of these images; the consequences for capric acid impregnation are quantified in Section “[Pore structure evolution with pyrolysis temperature](#)” (accessible pore volume) and section “[Phase change behavior and encapsulation efficiency](#)” (encapsulation efficiency and phase change enthalpy).

The elemental composition and surface chemical identity of the biochars were further investigated by energy dispersive X-ray spectroscopy. Figure 3 presents the EDS elemental maps of CSB 5.5, CSB 7.0, CSB 8.5 and CSB 10 (Fig. 3a–d, respectively), acquired by area mapping rather than by point analysis so that the quantification averages over a representative field rather than over a single spot. Carbon, nitrogen and oxygen are distributed uniformly over the particle in every sample, with no segregated heteroatom-rich domains, and the carbon signal strengthens progressively with pyrolysis temperature, consistent with the increasing degree of carbonization^{41,42}.

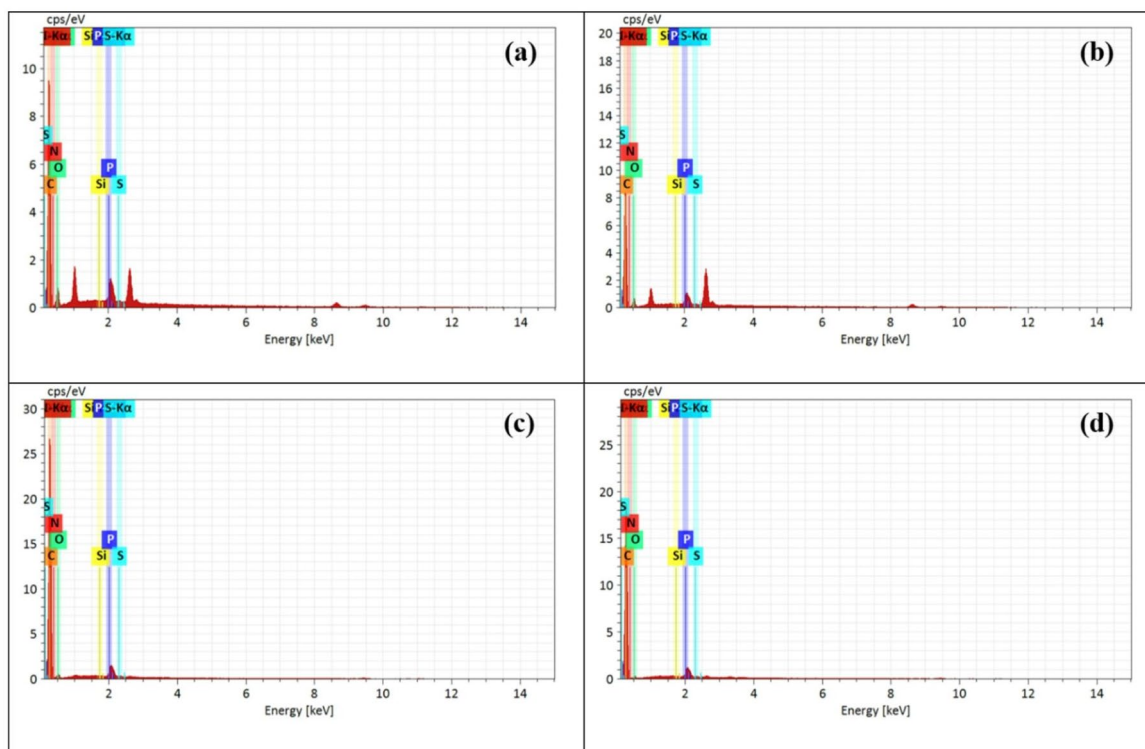


Fig. 3 EDS elemental maps of (a) CSB 5.5, (b) CSB 7.0, (c) CSB 8.5 and (d) CSB 10, acquired by area mapping at 15 kV and 2000× magnification. Characteristic peaks for carbon (C), oxygen (O), nitrogen (N), phosphorus (P), silicon (Si), and sulfur (S) are labelled.

Oxygen is detected in all four samples, arising from residual oxygen-containing functional groups that persist even after high-temperature treatment; its intensity decreases monotonically from CSB 5.5 to CSB 10, indicating the gradual loss of hydroxyl, carboxyl and other oxygenated species as the pyrolysis temperature rises^{9,25}. Silicon is detected at trace level in all four samples, originating from phytoliths inherently present in coconut shell biomass⁴³. The silicon signal remains weak in every sample, consistent with the trace amounts listed in Table 1. Phosphorus and sulfur are likewise detected throughout, reflecting the elemental composition inherited from the original lignocellulosic feedstock⁴⁴. The spectra recorded alongside the maps carry weak zinc (Zn L α at 1.01 keV, Zn K α at 8.64 keV) and chlorine (Cl K α at 2.62 keV) signals for CSB 5.5 and CSB 7.0, and none for CSB 8.5 or CSB 10. Zinc and chlorine were not included in the element list and are not quantified here, but their appearance indicates that a trace of the ZnCl₂ activating agent survives the post-pyrolysis acid wash in the two lower-temperature chars. This is the expected behaviour: ZnCl₂ boils at 732 °C, so that at 850 and 1000 °C it is volatilized during pyrolysis itself and none remains for the wash to remove, whereas below that temperature a small fraction is retained in regions the wash does not reach. No crystalline zinc phase is detected by X-ray diffraction in any of the four samples (section “[Surface chemistry and structural ordering](#)”). Residual zinc is undesirable because zinc species can catalyze degradation of capric acid during thermal cycling²⁶. The amounts indicated here are close to the detection limit and are confined to the two lower-temperature supports; no zinc is detected in CSB 8.5 or CSB 10, and the thermal cycling data of section “[Leakage resistance, thermal cycling stability, and photothermal response](#)” show no loss of stored enthalpy in any of the composites over repeated melt–freeze cycles.

The biochar yield decreases monotonically from 40.6% at 550 °C to 34.2, 27.6 and 23.7% at 700, 850 and 1000 °C respectively (Table 1), reflecting the progressive release of volatiles and the increasing extent of carbon burn-off with temperature. The quantitative elemental composition derived from the EDS area maps is summarized in Table 1, together with the 3 σ absolute errors reported by the instrument. Carbon is the dominant element in all samples, increasing from 65.96 mass% in CSB 5.5 to 74.18 mass% in CSB 10, reflecting progressive carbonization and the loss of heteroatoms during pyrolysis^{45,46}. Oxygen content falls from 15.73 to 3.52 mass% over the same range, confirming the removal of oxygen-containing functional groups. Nitrogen is returned as 15.89 to 20.75 mass%, far above the nitrogen inventory reported for lignocellulosic chars⁴⁴. This value is not treated here as a measurement of nitrogen content, for the reason set out in the following paragraph. Phosphorus (2.23–1.43 mass%), sulfur (0.18–0.07 mass%) and silicon (0.01–0.04 mass%) are inherited from the original biomass⁶. Silicon is present as phytolith-derived silica, which is retained because it melts above 1600 °C and is not dissolved by the dilute hydrochloric acid wash; its crystalline quartz component is detected independently by XRD (section “[Surface chemistry and structural ordering](#)”) and by the Si–O bands at 885 and 710 cm^{−1} in the FTIR spectra.

These figures require an explicit caveat. The 3 σ absolute errors returned by the instrument are $\pm 23.71\%$ points on carbon and ± 9.69 on nitrogen for CSB 5.5, and are of comparable magnitude for the other three samples; the measurement is in effect reporting that it cannot determine these quantities. The reason is intrinsic to the technique rather than particular to this instrument. The characteristic lines of carbon, nitrogen and oxygen all lie below approximately 0.6 keV, where they are poorly resolved and where absorption corrections in a low-atomic-number matrix are large, so that the photon budget in this region is apportioned among the three elements by a deconvolution that is under-determined and whose outcome depends on which elements are offered to the fitting routine. The nitrogen content noted above illustrates the point directly: even allowing for the concentration of involatile elements as 59 to 76% of the feedstock mass is lost during pyrolysis, a coconut shell char cannot contain 15.89 to 20.75 mass% nitrogen. What the data do establish is which elements are present and the direction in which each changes with pyrolysis temperature. Oxygen falls monotonically across the series, a trend corroborated independently by the loss of the O–H and C=O bands in the FTIR spectra (Sect. 3.5) and by the disappearance of the 11.2° reflection above 850 °C (section “[Surface chemistry and structural ordering](#)”). It is this trend, and not any absolute composition, on which the arguments of this work rest.

Energy-dispersive spectroscopy reports elemental abundance but not chemical state, and for the reasons set out above the light-element abundances it returns here are not quantitative. The following assignments are therefore offered as the speciation expected of a lignocellulosic char rather than as speciation established by these data.

Nitrogen originates from residual protein and free amino acids in the shell and adhering coir; during pyrolysis, amide and amine nitrogen converts first to pyrrolic (N-5) and then to pyridinic (N-6) forms, and above approximately 800 °C to quaternary or graphitic nitrogen (N-Q) substituted directly for carbon within the graphene layers, which is thermally stable above 1000 °C. Sulfur derives from cysteine and methionine residues and from inorganic sulfate, the labile thiol, sulfide and sulfate pools being removed below approximately 600 °C and thiophenic sulfur incorporated into the aromatic framework persisting beyond 900 °C. No argument in this work rests on the nitrogen inventory or on its trend with temperature, and confirmation of these assignments would require X-ray photoelectron spectroscopy of the N 1s and S 2p regions.

The morphological and compositional trends observed across the four biochars reveal a non-linear evolution with pyrolysis temperature. They also indicate that BET surface area alone, which we report in the following section, will not suffice to predict the effectiveness of each biochar as a support for capric acid. The accessibility of the pore network is expected instead to play the decisive role in determining PCM loading and thermal storage efficiency, and because that accessibility is governed by features far below the resolution of Fig. 2 it is established in section “[Pore structure evolution with pyrolysis temperature](#) and 3.3 rather than here^{9,26}.

Pore structure evolution with pyrolysis temperature

The textural properties of the ZnCl₂-activated coconut shell biochars were characterized by nitrogen adsorption-desorption analysis at 77 K, and the proposed pore structure evolution across pyrolysis temperatures is schematically illustrated in Fig. 4. Figure 5 presents the N₂ adsorption-desorption isotherms of CSB 5.5, CSB 7.0, CSB 8.5 and CSB 10. All four samples exhibit isotherms that can be classified as Type IV according to the IUPAC classification, characteristic of mesoporous materials⁴⁷. At low relative pressures ($P/P_0 < 0.1$), a steep increase in adsorbed volume is observed for CSB 7.0, CSB 8.5 and CSB 10, indicating the presence of micropores. In contrast, CSB 5.5 shows a much lower uptake in this region, reflecting its poorly developed microporosity. As the relative pressure increases, all samples display a gradual uptake followed by a distinct hysteresis loop in the range $P/P_0 = 0.4–0.9$. The shape of the hysteresis loop provides insight into the pore geometry. CSB

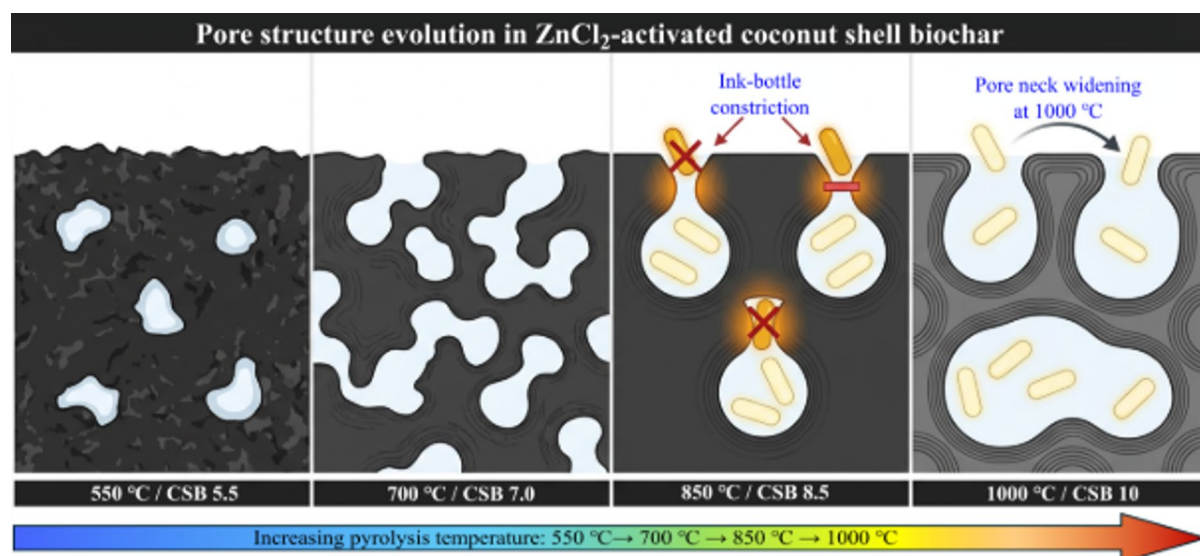


Fig. 4 Conceptual model of pore structure evolution in ZnCl₂-activated coconut shell biochar across pyrolysis temperatures (550–1000 °C). Yellow elongated shapes represent capric acid molecules; amber-orange highlights mark constricted pore necks at which ingress of the melt is impeded (CSB 8.5). The schematic is a model consistent with the sorption and electron microscopy data of sections “[Pore structure evolution with pyrolysis temperature](#)” and “[Nanoscale pore-wall architecture by HRTEM and SAED](#)” and is not a depiction of an observed structure; it is not drawn to scale.

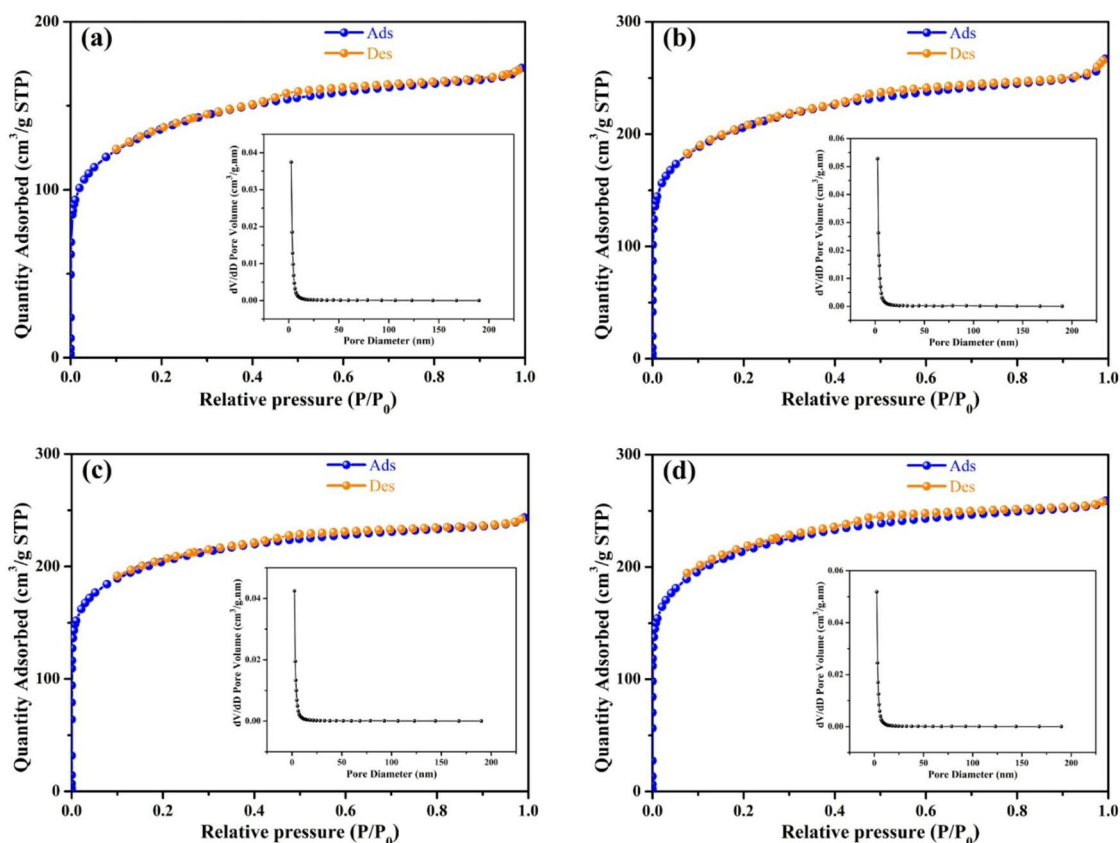


Fig. 5 N₂ adsorption-desorption isotherms of (a) CSB 5.5, (b) CSB 7.0, (c) CSB 8.5 and (d) CSB 10 measured at 77 K. The insets show the corresponding BJH pore size distributions (adsorption branch).

5.5 and CSB 7.0 exhibit H4-type hysteresis, which is commonly associated with narrow slit-shaped pores or constricted pore networks⁴⁸. CSB 8.5 shows a mixed H4/H2-type hysteresis. The H2 component is associated with desorption controlled by the pore neck rather than by the cavity, and is taken here as one indicator among several of constricted pore entrances rather than as proof of a particular pore geometry^{49,50}. CSB 10 displays a more pronounced H4 hysteresis with a sharper desorption branch, consistent with less constricted entrances after the higher-temperature treatment.

The proposed mechanism of pore structure evolution with pyrolysis temperature is schematically illustrated in Fig. 4, which integrates the textural data with the structural evolution of the carbon framework. At 550 °C, incomplete thermal decomposition of the lignocellulosic matrix yields a dense carbon framework with sparse, isolated pores and a correspondingly low accessible pore volume. Raising the temperature to 700 °C promotes extensive volatile release and ZnCl₂-driven dehydration, generating a well-connected open mesopore network in which the accessible pore volume rises. The BJH adsorption cumulative volumes of CSB 5.5 and CSB 7.0 could not be determined because the low-pressure branch of the isotherm was under-sampled (Table 2), so the comparison between 550 and 700 °C is drawn qualitatively. At 850 °C, however, localized partial melting of the carbon skeleton followed by re-solidification narrows a significant fraction of the pore entrances while preserving the larger internal cavities, consistent with the H2 hysteresis component. This constriction reduces the BJH adsorption volume to 0.1102 cm³g⁻¹ despite the BET surface area remaining high at 734.61 m²g⁻¹, indicating that a substantial fraction of the internal pore volume is not accessible to the molten capric acid. Further treatment at 1000 °C promotes structural ordering and thermal etching of the constricted necks, restoring pore accessibility and yielding a BJH adsorption volume of 0.1296 cm³g⁻¹ alongside the highest BET area of 758.73 m²g⁻¹. This non-monotonic evolution of accessible pore volume, open at 700 °C, constricted at 850 °C, and reopened at

Table 2 Textural properties of ZnCl₂-activated coconut shell biochars prepared at different pyrolysis temperatures.

Sample	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Mean pore diameter (nm)	BJH adsorption cumulative pore volume (cm ³ g ⁻¹)	MP micropore volume (cm ³ g ⁻¹)
CSB 5.5	481.98	0.2663	2.21	n.d.	n.d.
CSB 7.0	729.19	0.4109	2.25	n.d.	n.d.
CSB 8.5	734.61	0.3762	2.05	0.1102	0.369
CSB 10	758.73	0.3995	2.11	0.1296	0.3923

n.d. = not determined.

1000 °C, is the mechanistic basis for the encapsulation efficiency trend observed in the shape-stabilized composites and constitutes the central finding of the present work.

A detailed summary of the textural parameters derived from the isotherms is provided in Table 2. The BET surface area increases from 481.98 m² g⁻¹ for CSB 5.5 to 729.19 m² g⁻¹ for CSB 7.0, then slightly to 734.61 m² g⁻¹ for CSB 8.5, and finally to 758.73 m² g⁻¹ for CSB 10. The total pore volume (measured at P/P₀ = 0.990) follows a similar trend: 0.2663 cm³ g⁻¹ (CSB 5.5), 0.4109 cm³ g⁻¹ (CSB 7.0), 0.3762 cm³ g⁻¹ (CSB 8.5) and 0.3995 cm³ g⁻¹ (CSB 10). The mean pore diameter, calculated by the BJH method from the adsorption branch, varies only slightly across the series, from 2.21 nm (CSB 5.5) to 2.25 nm (CSB 7.0), 2.05 nm (CSB 8.5) and 2.11 nm (CSB 10). These values place the biochars in the mesoporous range, which is favorable for PCM confinement, as pores smaller than 2 nm would severely restrict molecular motion and suppress crystallization^{51,52}.

The mean pore diameter is similar for all four biochars, lying between 2.05 and 2.25 nm, and this similarity should not be read as evidence against a change in pore-neck geometry. The mean diameter is a volume-weighted average over the entire distribution and is structurally insensitive to the property at issue for three reasons. It reports the size of the cavities rather than of the entrances, so that two pore systems with identical means may differ completely in connectivity. It is numerically dominated by the large population of narrow pores, so that a change confined to the pore mouths displaces it very little. And it is measured with a probe molecule that is not the working fluid: nitrogen at 77 K has a kinetic diameter of 0.36 nm and passes freely through necks that exclude a hydrogen-bonded capric acid dimer of approximately 2.7 nm extended length, so that a pore counted as accessible to nitrogen may be entirely closed to the melt. It is for this reason that the accessible pore volume determined on the adsorption branch, rather than the mean pore diameter or the BET surface area, is used throughout this work as the predictor of PCM loading.

A critical observation emerges when the total pore volume is compared with the cumulative pore volume derived from the BJH adsorption branch. For CSB 8.5 the BJH adsorption cumulative pore volume is 0.1102 cm³ g⁻¹, substantially lower than the total pore volume of 0.3762 cm³ g⁻¹, indicating that a large fraction of the pore volume is not reached through the entrances that are open during the adsorption measurement. For CSB 10 the corresponding value is 0.1296 cm³ g⁻¹ against a total pore volume of 0.3995 cm³ g⁻¹. The MP analysis gives micropore volumes of 0.369 and 0.3923 cm³ g⁻¹ for CSB 8.5 and CSB 10 respectively, in both cases close to the total pore volume, confirming that the porosity is predominantly narrow in both samples.

By the conventional metrics the two samples are closely similar. Their BET surface areas differ by only 3.3% (734.61 against 758.73 m² g⁻¹), a difference within the reproducibility of the measurement, and their isotherms are broadly similar in form. This similarity is not incidental to the argument of this paper but is its premise: the BET surface area does not distinguish between these two supports, and any expectation of performance founded on it would predict that they behave alike. The same failure is more pronounced for CSB 7.0, which possesses 96.1% of the BET area of CSB 10 yet delivers only 74.1% of its encapsulation efficiency. The quantity that does distinguish them is the pore volume accessible on the adsorption branch, which rises by 17.6% from 0.1102 to 0.1296 cm³ g⁻¹. The capric acid encapsulation efficiency rises by 18.5% over the same pair, from 57.59 to 68.25%, and the independent gravimetric estimate from TGA rises by 17.9%, from 56.26 to 66.37 wt%. The accessible pore volume and the two independent measures of PCM loading therefore agree to within 1% point, while the total surface area remains essentially unchanged. We do not claim on this basis that the two supports possess categorically different pore systems; we claim that the small difference between them resides in the accessible

fraction rather than in the total internal surface, and that it is the accessible fraction that governs performance. The structural origin of this difference is established directly by high-resolution electron microscopy in section “[Nanoscale pore-wall architecture by HRTEM and SAED](#)”.

The MP method and the BJH cumulative volume on the adsorption branch both require numerical differentiation of a densely sampled low-pressure isotherm ($P/P_0 < 0.1$). The low-pressure branches for CSB 5.5 and CSB 7.0 were acquired with an insufficient point density for a stable derivative, and values are therefore not reported rather than being quoted from an under-sampled branch. The BET surface area, total pore volume and mean pore diameter are obtained without differentiation and are unaffected. The principal comparison of this work, between CSB 8.5 and CSB 10, was measured under identical fully sampled conditions.

The evolution of pore accessibility with pyrolysis temperature can be rationalized by the competing processes of carbonization and structural rearrangement. At 550 °C, incomplete decomposition leaves a rigid but poorly porous char. At 700 °C, the release of volatiles creates a relatively open mesoporous network. As the temperature reaches 850 °C, partial melting of the carbon skeleton can occur, followed by re-solidification that narrows pore entrances while preserving larger internal cavities^{25,32}. This is reflected in the low BJH adsorption volume of CSB 8.5 and is imaged directly by high-resolution electron microscopy in section “[Nanoscale pore-wall architecture by HRTEM and SAED](#)”. At 1000 °C, further thermal treatment promotes graphitization and structural ordering, which appears to widen the pore necks, thereby improving accessibility. Similar behavior has been reported for other biomass-derived activated carbons^{23,26}.

The practical implication is direct: when capric acid is introduced as a molten PCM, its ability to penetrate the pore network is governed by the accessible pore volume, not the total pore volume. A biochar with a high BET surface area but constricted pores (CSB 8.5) will retain less PCM than a biochar with a similar or even slightly lower BET area but open pores (CSB 7.0 and CSB 10). This distinction forms the central hypothesis of the present work and is systematically examined in the following sections through thermal analysis of the shape-stabilized composites.

Nanoscale pore-wall architecture by HRTEM and SAED

Because scanning electron microscopy cannot resolve the pore necks that this study identifies as the controlling feature, the biochars were examined by high-resolution transmission electron microscopy and selected-area electron diffraction (Fig. 6). Imaging was performed on the two high-temperature biochars, CSB 8.5 and CSB 10, between which the anomalous encapsulation behaviour occurs and which are the subject of the mechanistic question addressed here, together with CSB 7.0. The last of these was selected in preference to CSB 5.5 because it is the sample that most sharply exposes the failure of surface area as a predictor: it possesses 96.1% of the BET area of CSB 10 while delivering only 74.1% of its encapsulation efficiency, and it therefore provides the low-temperature reference state against which the onset of structural ordering is judged. Lattice-fringe parameters were extracted by Fourier analysis of the calibrated images following established practice for turbostratic carbons³⁷ and are collected in Table 3.

At 700 °C (Fig. 6a–d) the material is a dense, essentially featureless amorphous carbon. No lattice fringes are resolved even at the highest magnification (Fig. 6c), and the SAED pattern (Fig. 6d) consists of a single broad halo, confirming the absence of coherent stacking⁵³. Fourier analysis yields no well-defined (002) periodicity, with an ill-defined maximum near 0.47 nm and a stacking coherence length below 0.5 nm. This is consistent with the limited degree of aromatic ring condensation reported for biomass chars prepared below 800 °C⁵⁴.

At 850 °C (Fig. 6e–h) short, strongly curved graphene fringes appear. Fourier analysis gives $d_{002} = 0.346\text{--}0.370$ nm and a stacking coherence length L_c of approximately 1.0–1.1 nm, corresponding to about three stacked layers. Critically, these fringes are not mutually parallel: they curl and close upon themselves, forming near-circular envelopes such as the one outlined in Fig. 6f, which encloses a cavity of roughly 20–25 nm with no opening visible in projection. Curved and closed fringe architectures of this kind are characteristic of non-graphitizing carbons, in which non-hexagonal defects impose curvature on the graphene sheets and prevent parallel stacking^{55,56}.

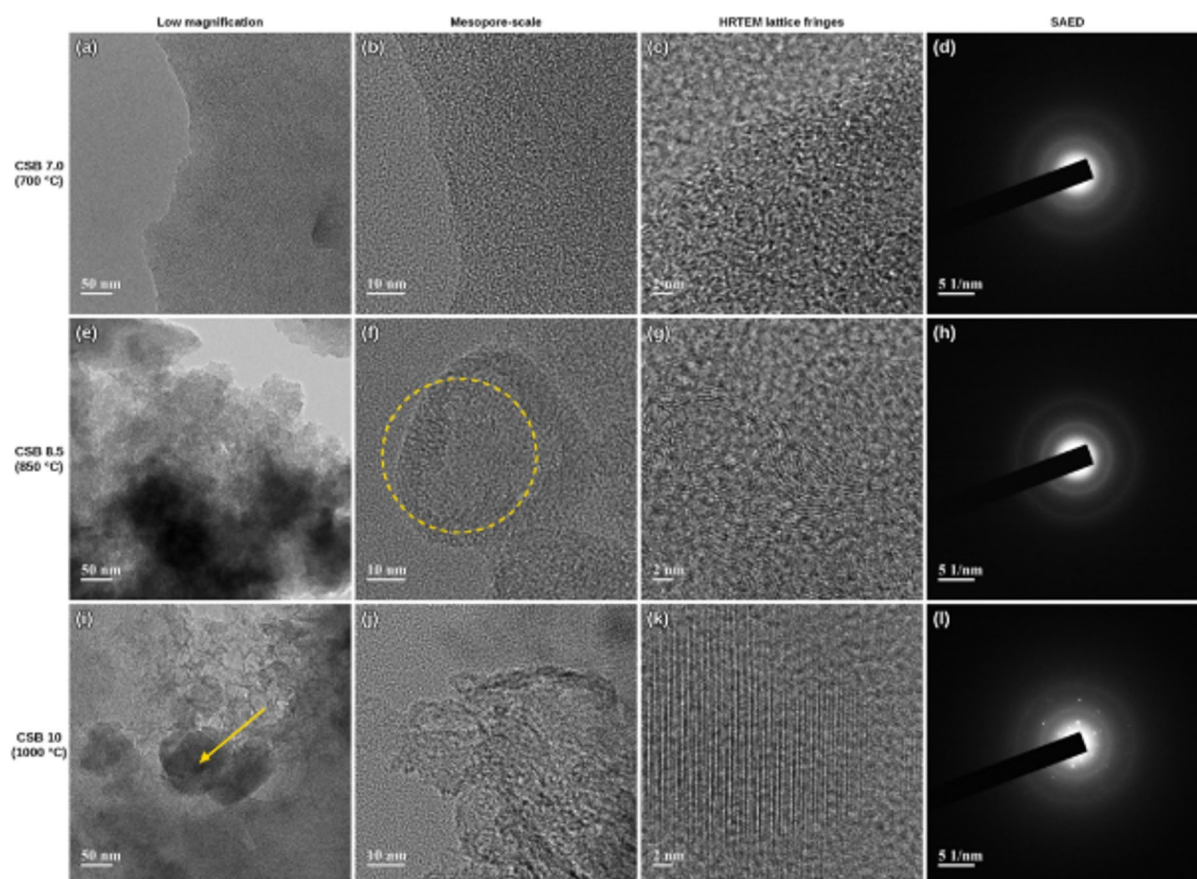


Fig. 6 High-resolution TEM and selected-area electron diffraction of the ZnCl_2 -activated coconut shell biochars. (a–d) CSB 7.0, (e–h) CSB 8.5, (i–l) CSB 10. Columns, left to right: low-magnification bright-field image, mesopore-scale image, high-resolution lattice-fringe image, and SAED pattern. The dashed circle in (f) outlines a closed, curved fringe envelope enclosing a cavity of approximately 20–25 nm with no opening visible in projection. The arrow in (i) indicates a cavity with a wide, unobstructed mouth. Note in (k) the extended, mutually parallel fringe stacks of CSB 10 in contrast to the short, curved and mutually disordered fringes of CSB 8.5 in (g), and the appearance of discrete diffraction spots in (l) that are absent in (h) and (d). Scale bars are marked on each panel.

Table 3 Lattice-fringe parameters of the ZnCl_2 -activated coconut shell biochars determined by Fourier analysis of the HRTEM images.

Sample	d_{002} (nm)	L_c (nm)*	Approx. stacked layers	SAED
CSB 7.0	Not well defined (broad maximum near 0.47)	<0.5	Not resolvable	Single broad halo
CSB 8.5	0.346–0.370	1.0–1.1	≈3	Diffuse rings
CSB 10	0.336	1.9–3.2	≈6–10	Diffuse rings with discrete spots

* L_c estimated from the radial width of the (002) maximum in the Fourier transform of calibrated lattice-fringe images; values are averages over two or more independent regions per sample.

The SAED pattern (Fig. 6h) remains a set of diffuse rings. This fringe architecture provides a direct structural origin for the constricted pore entrances inferred from the sorption data in section “[Pore structure evolution with pyrolysis temperature](#)”, since curved, self-closing layers terminate a pore mouth rather than lining an open channel.

At 1000 °C (Fig. 6i–l) the fringes straighten and coalesce into extended, mutually parallel stacks (Fig. 6k) with $d_{002}=0.336$ nm, close to the 0.3354 nm interlayer spacing of graphite, and $L_c = 1.9\text{--}3.2$ nm, that is six to ten stacked layers. The SAED pattern (Fig. 6l) now shows discrete diffraction spots superimposed on the diffuse rings, confirming the emergence of nanocrystalline ordered domains. Parallel stacking generates straight, slit-shaped interlayer and inter-stack channels in place of the closed curved envelopes of the 850 °C sample, and the low-magnification image (Fig. 6i) correspondingly shows a cavity with a wide, unobstructed mouth (arrowed).

The transition from short curved fringes forming closed envelopes at 850 °C to extended parallel stacks bounding open channels at 1000 °C constitutes direct nanoscale evidence for the pore-neck widening proposed in Fig. 4 and complements the sorption evidence of section “[Pore structure evolution with pyrolysis temperature](#)”. It is consistent with the modest 3.3% increase in BET surface area between the two samples, which reflects the total internal surface, alongside the much larger 17.6% increase in BJH adsorption cumulative pore volume and the 18.5% increase in capric acid encapsulation efficiency, both of which reflect the fraction of that surface the melt can actually reach.

Surface chemistry and structural ordering

The chemical functionality and structural evolution of the CSB biochars were investigated by FTIR spectroscopy and XRD. The FTIR spectra of CSB 5.5, CSB 7.0, CSB 8.5 and CSB 10 are shown in Fig. 7a. All spectra exhibit absorption bands characteristic of oxygen-containing functional groups, aromatic carbon structures and siliceous residues. The detailed assignment of each band, along with the corresponding wavenumber and cause of absorption, is summarized in Table 4. In brief, a broad O–H stretching band around 3400 cm^{-1} decreases in intensity with increasing pyrolysis temperature, indicating progressive dehydration and loss of surface hydroxyl groups. The C–H stretching bands near $3020\text{--}2970\text{ cm}^{-1}$, prominent in CSB 5.5, are almost completely lost by 1000 °C, confirming the extensive aromatization of the carbon framework. The weak absorption remaining in CSB 10 is not assigned to aliphatic hydrocarbon, which would not be expected to survive treatment at this temperature, but to aromatic C–H at the edges of the polyaromatic domains and to adventitious hydrocarbon adsorbed from the laboratory atmosphere, to which a biochar of $759\text{ m}^2\text{ g}^{-1}$ is particularly susceptible and which the surface-sensitive ATR geometry preferentially samples. The C=O stretching band near 1735 cm^{-1} , prominent in CSB 5.5, weakens significantly at 1000 °C due to decarboxylation. Conversely, the aromatic C=C band near

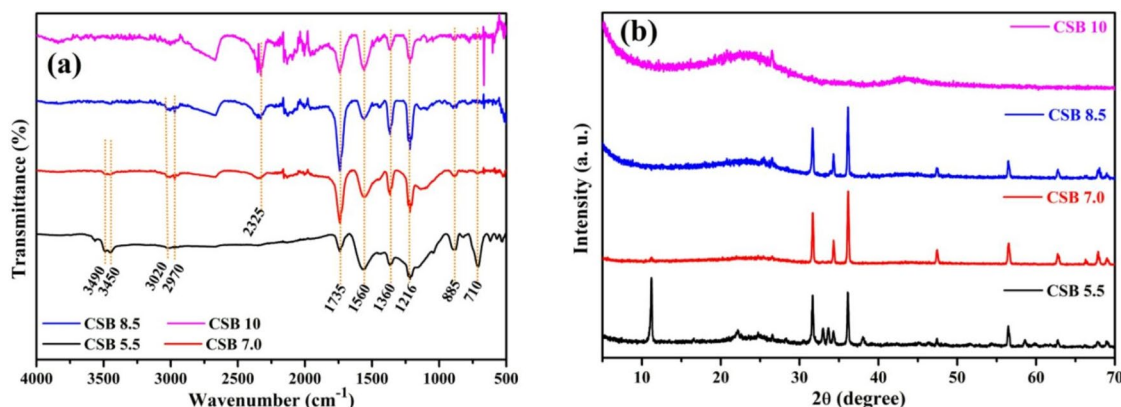


Fig. 7 (a) FTIR spectra, (b) XRD of CSB 5.5, CSB 7.0, CSB 8.5 and CSB 10.

Table 4 FTIR band assignments for CSB 5.5, CSB 7.0, CSB 8.5 and CSB 10.

Wavenumber (cm ⁻¹)	Assigned band	Cause of absorption	Ref.
3399–3450	O–H stretching	Hydroxyl groups / adsorbed water	57–60
3020–2970	Aromatic and residual aliphatic C–H stretching	Aromatic edge C–H and residual aliphatic hydrocarbon; weakens sharply with pyrolysis temperature and is close to the baseline in CSB 10	61–63
2325	CO ₂ absorption	Atmospheric CO ₂ artifact	64,65
1735	C = O stretching	Carboxyl/ester groups	66,67
1560	Aromatic C = C	Aromatic carbon formation	68
1360	Aromatic C–H in-plane deformation and symmetric C–O stretching	Edge-site aromatic C–H together with phenolic and carboxylate C–O	68,69
1216	N–H deformation	Amine-related vibrations	17,67
885	Si–O bending	Silicate network	70,71
710	Si–O vibration	Quartz phase	71,72

1560 cm⁻¹ becomes more pronounced with temperature, reflecting the growth of polyaromatic domains. Strong Si–O bands near 885 cm⁻¹ and 710 cm⁻¹ persist in all samples, confirming that quartz-derived silica remains as a stable inorganic component. The N–H deformation at 1216 cm⁻¹ indicates a residual population of edge-bound nitrogen, consistent with the nitrogen speciation discussed in Sect. 3.1. No bands corresponding to zinc species are observed, consistent with the absence of metallic or oxidized zinc peaks in the EDS spectra and XRD patterns.

The XRD patterns of the four biochars are presented in Fig. 7b over the 2θ range of 5–70°. All samples exhibit a broad, low-intensity hump centered near 2θ = 24–26°, which corresponds to the (002) reflection of turbostratic carbon. This feature indicates the predominance of disordered or amorphous carbon structures with only limited short-range graphitic order^{73–76}. The absence of a sharp graphite peak at 2θ ≈ 26.4° confirms that the biochars remain predominantly non-graphitic even after treatment at 1000 °C. Superimposed on the amorphous carbon background, several weak but distinct diffraction peaks are observed at 2θ = 26.5°, 38.0°, 47.5°, 56.5°, 66.3°, 67.9° and 69.0°. These peaks are indexed to crystalline quartz (SiO₂) based on the ICDD PDF #46-1045 reference pattern. The presence of quartz is attributed to phytolith silica inherently present in the original coconut shell biomass, which remains thermally stable during pyrolysis and chemical activation^{77–79}. The intensity of the quartz reflections does not vary systematically with pyrolysis temperature, indicating that the silica phase is largely unaffected by the activation and washing procedures.

A distinct reflection is observed at 2θ = 11.2°, corresponding to an interplanar spacing of 0.79 nm. Its intensity depends strongly on pyrolysis temperature: it is prominent in CSB 5.5, very weak in CSB 7.0, and absent in both CSB 8.5 and CSB 10. Spacings of this magnitude, approximately twice the 0.335 nm interlayer distance of graphite, are characteristic of layered carbons in which the interlayer galleries are held apart by oxygen-containing functional groups; in graphite oxide the corresponding (001) reflection appears near 11° and collapses to approximately 0.366 nm once these groups are removed⁸⁰. No oxidation step is employed in the present synthesis, and the reflection is therefore attributed not to graphite oxide itself but to residual oxygen-bridged expanded domains retained in the incompletely carbonized low-temperature char, which are eliminated thermally as carbonization proceeds. This assignment is consistent with the FTIR spectra, in which the C = O band at 1735 cm⁻¹ and the O–H band near 3400 cm⁻¹ are most intense for CSB 5.5 and weaken markedly with temperature, and with the concurrent development of the broad (002) turbostratic reflection at 24–26°. Taken together with the interlayer spacings of 0.346–0.370 nm at 850 °C and 0.336 nm at 1000 °C determined by HRTEM (Table 3, section “[Nanoscale pore-wall architecture by HRTEM and SAED](#)”), the data trace a continuous contraction of the interlayer distance from 0.79 to 0.336 nm across the series. The reflection tracks interlayer rather than total oxygen, since CSB 7.0 retains a total oxygen content comparable to that of CSB 5.5 (14.11 against 15.73 mass%, Table 1) while the

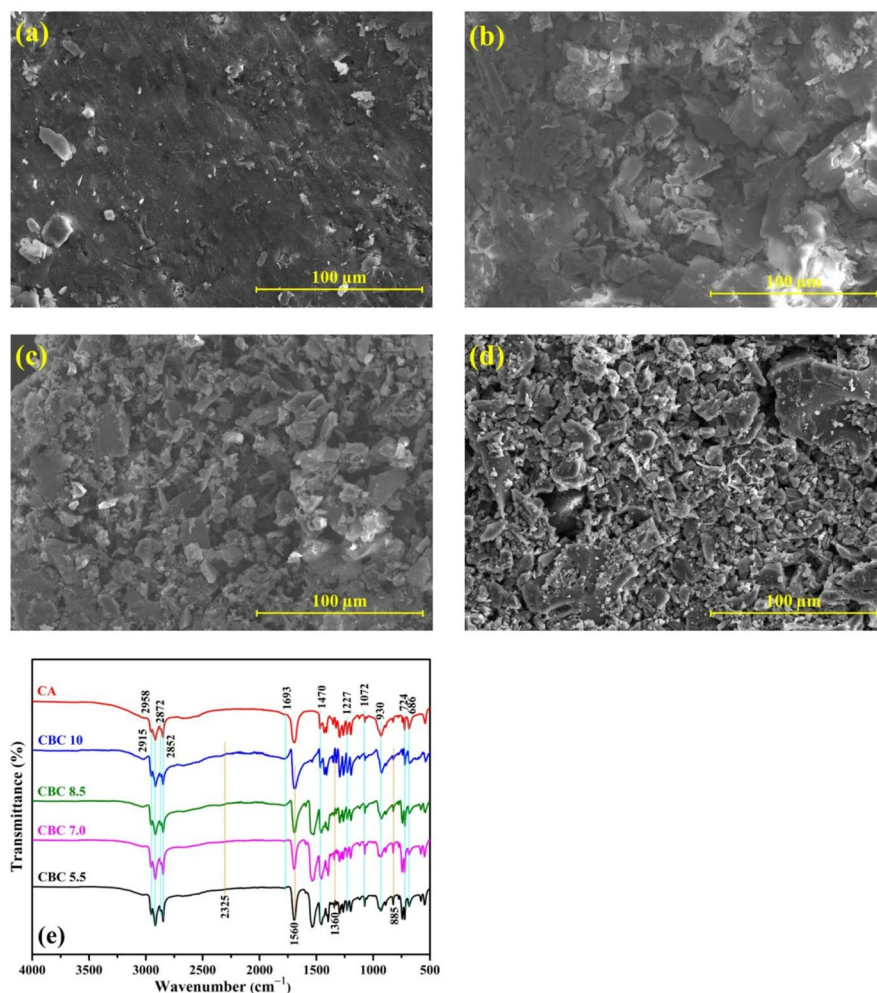
reflection has almost disappeared, indicating that bridging groups within the galleries are removed before edge-bound oxygen. A minor additional contribution from a thermally labile hydrated mineral phase inherited from the biomass ash cannot be excluded. No reflection attributable to metallic zinc, ZnO or ZnCl₂ is observed at any angle in any of the four patterns.

The combined FTIR and XRD results demonstrate that increasing pyrolysis temperature progressively removes oxygen-containing functional groups, promotes the formation of aromatic carbon networks, and preserves the intrinsic quartz phase. The absence of crystalline carbon or residual activating agent impurities, together with the chemically stable siliceous residues, creates a favorable environment for the subsequent confinement of capric acid within the biochar pore network.

Morphology and chemical compatibility of shape-stabilized PCM composites

The success of CA impregnation into the four biochars was evaluated by SEM. Figure 8(a-d) shows the surface morphology of the resulting composites CBC 5.5, CBC 7.0, CBC 8.5 and CBC 10. In CBC 5.5 (Fig. 8a), the surface appears relatively smooth with only occasional shallow irregularities, suggesting that capric acid has largely covered the biochar. However, the moderate uniformity reflects the limited total pore volume of CSB 5.5 (0.2663 cm³ g⁻¹, Table 2), which restricts the amount of PCM that can be retained. CBC 7.0 (Fig. 8b) exhibits a smoother and more homogeneous surface than CBC 5.5, with few discernible features. This observation is consistent with

Fig. 8 SEM images of shape-stabilized PCM composites: (a) CBC 5.5, (b) CBC 7.0, (c) CBC 8.5, (d) CBC 10; (e) FTIR spectra of pure capric acid and CBC 5.5, CBC 7.0, CBC 8.5 and CBC 10.



the higher total pore volume of CSB 7.0 ($0.4109\text{ cm}^3\text{ g}^{-1}$) and its open, well-connected pore network, which allows capric acid to spread uniformly.

CBC 8.5 (Fig. 8c) shows a distinctly heterogeneous surface: some areas are smooth, while others reveal a rougher texture with shallow depressions or residual pore outlines, indicating incomplete filling. This heterogeneity correlates directly with the constricted pore structure of CSB 8.5. Despite having a total pore volume of $0.3762\text{ cm}^3\text{ g}^{-1}$, the BJH adsorption cumulative pore volume is only $0.1102\text{ cm}^3\text{ g}^{-1}$ (Table 2), indicating that a large fraction of the pore volume is not accessible through the pore entrances. Consequently, the molten capric acid cannot fully penetrate the pore network, leaving parts of the biochar surface exposed. CBC 10 (Fig. 8d) displays the smoothest and most homogeneous surface among all samples, with almost no visible pores or cracks. This indicates near-complete impregnation, which is supported by the highest accessible pore volume of CSB 10 (BJH adsorption $0.1296\text{ cm}^3\text{ g}^{-1}$) and the open, well-connected pore network formed at $1000\text{ }^\circ\text{C}$. The correlation between the observed surface coverage and the thermal energy storage performance, including encapsulation efficiency and phase change enthalpy, is quantitatively addressed in Sect. 3.6.1.

The chemical compatibility between capric acid and the biochar supports was evaluated by Fourier transform infrared spectroscopy. Figure 8e presents the overlaid FTIR spectra of pure capric acid and the four CBC composites. Pure capric acid shows characteristic absorption bands at 2958 cm^{-1} (asymmetric $-\text{CH}_3$ stretching), 2915 cm^{-1} (asymmetric $-\text{CH}_2$ stretching), 2872 cm^{-1} (symmetric $-\text{CH}_3$ stretching), 2852 cm^{-1} (symmetric $-\text{CH}_2$ stretching), 1693 cm^{-1} ($\text{C}=\text{O}$ stretching), 1470 cm^{-1} (asymmetric $-\text{CH}_2$ bending), 1292 , 1265 and 1227 cm^{-1} ($\text{C}-\text{O}$ stretching), 1072 cm^{-1} ($\text{C}-\text{O}$ stretching), 930 cm^{-1} (out-of-plane $-\text{OH}$ bending), 885 cm^{-1} ($-\text{CH}_2$ rocking) and 724 cm^{-1} ($-\text{CH}$ rocking). All CBC composites exhibit the same set of absorption bands without any peak shifts or new bands, confirming that no chemical reaction occurs between capric acid and the biochar. The interaction remains purely physical (capillary forces, surface tension, van der Waals attractions), which is essential for reversible phase change cycling. The detailed band assignments are compiled in Table 5.

Thermal energy storage performance and thermal stability

Phase change behavior and encapsulation efficiency

The thermal energy storage performance of pure CA and the shape-stabilized composites CBC 5.5, CBC 7.0, CBC 8.5 and CBC 10 was characterized by differential scanning calorimetry. Figure 9a and b show the DSC thermograms for heating and cooling of all samples, and the extracted parameters are summarized in Table 6. Pure CA melts at $35.50\text{ }^\circ\text{C}$ with an enthalpy of fusion (ΔH_m) of 165.42 J g^{-1} and crystallizes at $24.25\text{ }^\circ\text{C}$ with an

Table 5 FTIR band assignments for pure capric acid and CBC composites.

Wavenumber (cm^{-1})	Assigned band	Cause of absorption	Ref.
2958	Asymmetric stretching	$-\text{CH}_3$	81,82
2915	Asymmetric stretching	$-\text{CH}_2$	81,82
2872	Symmetric stretching	$-\text{CH}_3$	82,83
2852	Symmetric stretching	$-\text{CH}_2$	81,82,84
1693	Stretching	$-\text{C}=\text{O}$	85
1470	Asymmetric bending	$-\text{CH}_2$	86
1292	Stretching	$-\text{C}-\text{O}$	87,88
1265	Stretching	$-\text{C}-\text{O}$	89
1227	Stretching	$-\text{C}-\text{O}$	90
1072	Stretching	$-\text{C}-\text{O}$	91
930	Out of plane bending	$-\text{OH}$	88
885	Rocking	$-\text{CH}_2$	92
724	Rocking	$-\text{CH}$	93
686	Out of plane bending	$-\text{COH}$	94

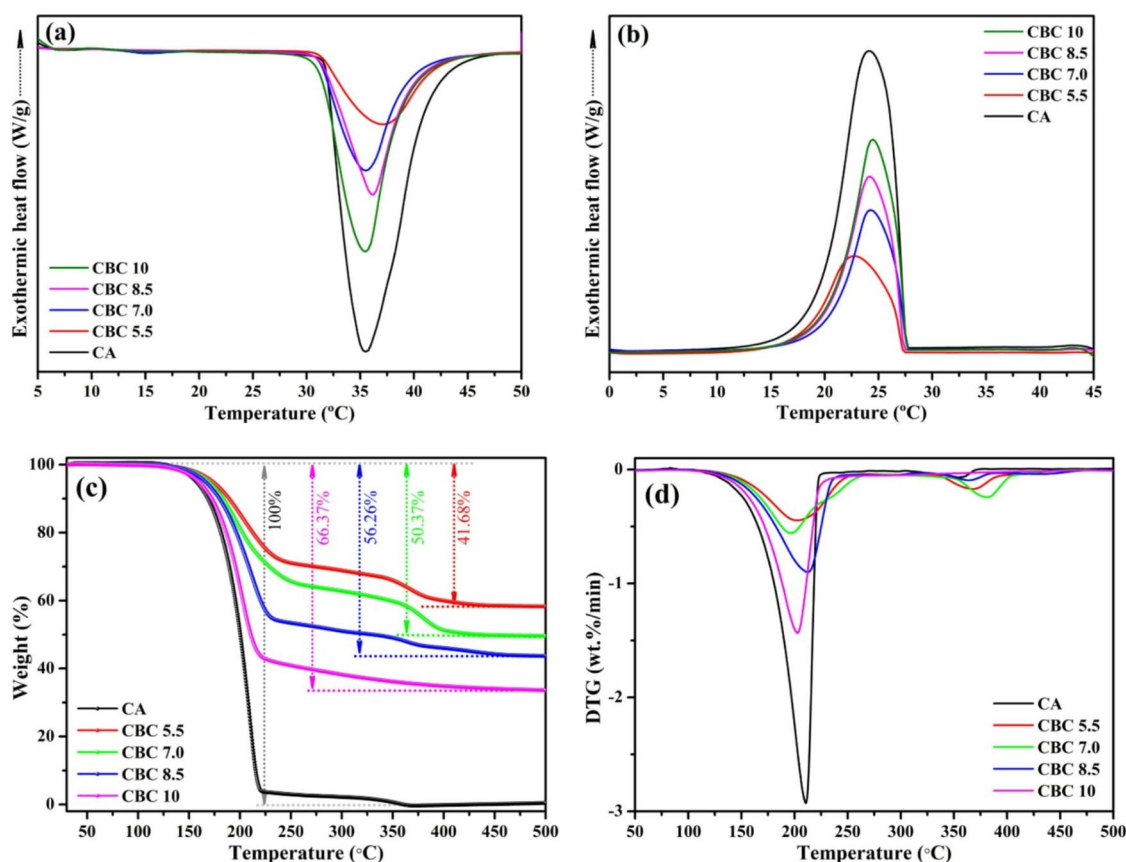


Fig. 9 Thermal characterization of pure capric acid and CBC composites: (a) DSC heating curves, (b) DSC cooling curves, (c) TGA curves, (d) DTG curves. Scanning rate for DSC was $10\text{ }^{\circ}\text{C min}^{-1}$.

Table 6 Phase change properties of pure capric acid and CBC composites.

Sample	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	T_s ($^{\circ}\text{C}$)	ΔH_s (J/g)	R (%)	E (%)
CA	35.50	165.42	24.25	166.34	-	-
CBC 5.5	37.25	69.92	22.75	70.99	42.25	42.48
CBC 7.0	35.50	83.64	24.25	85.43	50.57	50.97
CBC 8.5	36.24	95.26	24.33	97.09	57.59	57.99
CBC 10	35.62	112.88	24.49	114.61	68.25	68.58

enthalpy of crystallization (ΔH_s) of 166.34 J g^{-1} . All CBC composites exhibit single melting and single crystallization peaks, confirming that capric acid retains its solid-liquid phase transition without decomposition or the formation of multiple crystalline phases^{81,95}. The melting temperatures of the composites ($35.50\text{--}37.25\text{ }^{\circ}\text{C}$) are very close to that of pure CA, indicating that confinement within the biochar pores does not significantly alter the phase change temperature. The slight increase for CBC 5.5 ($37.25\text{ }^{\circ}\text{C}$) may be due to the restricted molecular mobility in smaller pores, which raises the energy barrier for melting^{51,96}.

The melting enthalpy increases progressively with the pyrolysis temperature of the biochar. CBC 5.5 gives $\Delta H_m = 69.92\text{ J g}^{-1}$, CBC 7.0 gives 83.64 J g^{-1} , CBC 8.5 gives 95.26 J g^{-1} and CBC 10 gives 112.88 J g^{-1} . The corresponding encapsulation efficiency (R %), defined as the ratio of the composite's ΔH_m to that of pure CA, follows the same trend: 42.25% (CBC 5.5), 50.57% (CBC 7.0), 57.59% (CBC 8.5) and 68.25% (CBC 10). The overall efficiency (E %), which averages the melting and crystallization enthalpies, shows nearly identical values,

confirming the consistency of the thermal cycling behavior. The $R\%$ ^{97,98} and the $E\%$ ^{19,99} are derived from the following equations:

$$R\% = \frac{\Delta H_{m, \text{ CBC composite}}}{\Delta H_{m, \text{ CA}}} \times 100 \quad (1)$$

$$E\% = \frac{(\Delta H_{m, \text{ CBC composite}} + \Delta H_{s, \text{ CBC composite}})}{(\Delta H_{m, \text{ CA}} + \Delta H_{s, \text{ CA}})} \times 100 \quad (2)$$

The encapsulation efficiency trend correlates with the pore accessibility evolution illustrated in Fig. 4 and quantified in Table 2, as discussed in section “Pore structure evolution with pyrolysis temperature”. CSB 5.5 has the lowest total pore volume ($0.2663 \text{ cm}^3 \text{ g}^{-1}$) and limited microporosity, which restricts CA loading. CSB 7.0 offers a higher total pore volume ($0.4109 \text{ cm}^3 \text{ g}^{-1}$) and an open pore network, leading to improved loading. CSB 8.5, despite having a similar BET surface area to CSB 7.0, develops constricted pore entrances (BJH adsorption volume only $0.1102 \text{ cm}^3 \text{ g}^{-1}$), yet its efficiency (57.59%) is still higher than that of CSB 7.0 (50.57%). This indicates that even partially accessible pores contribute to PCM retention, and the higher total pore volume of CSB 8.5 ($0.3762 \text{ cm}^3 \text{ g}^{-1}$) compared to CSB 7.0 may still allow more CA to be absorbed, albeit with incomplete pore filling. The highest efficiency for CSB 10 (68.25%) is achieved with the most open, well-connected pore network and the largest accessible pore volume (BJH adsorption $0.1296 \text{ cm}^3 \text{ g}^{-1}$).

Thermogravimetric analysis and actual PCM loading

The thermal stability and actual CA loading in the composites were evaluated by thermogravimetric analysis (TGA) under nitrogen atmosphere. Figure 9c and d show the TGA and derivative thermogravimetric (DTG) curves of pure CA and the four CBC composites. Pure CA undergoes a single-step decomposition between approximately 150°C and 250°C , with a maximum weight loss rate near 210°C , and leaves virtually no residue ($< 1 \text{ wt}\%$) at 500°C . All CBC composites exhibit a major weight loss in the same temperature range, corresponding to the volatilization and decomposition of CA. Above 250°C up to 500°C , the biochar matrix shows only a slight, gradual mass loss (less than $5 \text{ wt}\%$). This is expected because the biochars were already pyrolyzed at $550\text{--}1000^\circ\text{C}$; under inert nitrogen, no further decomposition occurs below the original pyrolysis temperature, and only residual hydrogen-containing groups or trapped fragments are eliminated. No additional decomposition step is observed, confirming that the biochar remains largely intact up to 500°C ^{26,100}. The onset temperature of capric acid decomposition in the composites (around $160\text{--}170^\circ\text{C}$) is slightly higher than that of pure CA ($\approx 130^\circ\text{C}$), indicating that confinement within the biochar pores delays thermal degradation^{10,25}.

The thermograms exhibit four distinct features, each with a separate origin. First, the decomposition onset shifts from approximately 130°C for pure capric acid to $160\text{--}170^\circ\text{C}$ for all composites; the vapour pressure above the concave meniscus of a nanoconfined liquid is reduced relative to a flat bulk surface, and the escaping molecules must additionally overcome the dispersion interaction with the pore walls and diffuse through a tortuous network, so that a higher temperature is required to reach the same evaporation rate. Second, the magnitude of the principal mass-loss step increases monotonically from 41.68 to $66.37 \text{ wt}\%$ with the pyrolysis temperature of the support, tracking the accessible pore volume and agreeing closely with the DSC encapsulation efficiencies. Third, the residue at 500°C falls from 58.32 to $33.63 \text{ wt}\%$ as the complement of the loading, the higher residues of the lower-temperature composites reflecting both their smaller PCM inventory and the greater proportion of incompletely carbonized, ash-bearing support. Fourth, the slow mass loss of less than $5 \text{ wt}\%$ between 250 and 500°C , which shows no discrete step, arises from the release of residual hydrogen-bearing edge groups and trapped pyrolysis fragments rather than from decomposition of the framework, since under nitrogen a biochar cannot decompose below the temperature at which it was formed. This loss is smallest for CBC 10, consistent with the decrease in oxygen content from 15.73 to $3.52 \text{ mass}\%$ across the series.

The residual mass at 500 °C is directly related to the biochar content and any inorganic residues (silica, etc.). The measured residual values are: 58.32 wt% for CBC 5.5, 49.63 wt% for CBC 7.0, 43.74 wt% for CBC 8.5, and 33.63 wt% for CBC 10. Correspondingly, the weight loss of the composites (attributed to capric acid decomposition) is 41.68 wt%, 50.37 wt%, 56.26 wt%, and 66.37 wt%, respectively. These weight loss values are in excellent agreement with the encapsulation efficiencies (R%) determined by DSC: 42.25% (CBC 5.5), 50.57% (CBC 7.0), 57.59% (CBC 8.5), and 68.25% (CBC 10). The slight differences (e.g., 41.68% vs. 42.25% for CBC 5.5) are within experimental error and confirm that the DSC-measured latent heat accurately reflects the actual mass fraction of capric acid that undergoes phase change. The higher residual mass for lower pyrolysis temperature biochars indicates that these composites contain more thermally stable inorganic residues (silica, etc.) and/or less complete carbonization of the biochar itself. All composites are thermally stable up to at least 150 °C, which is far above their intended operating temperature range (room temperature to approximately 40 °C for building thermal management). The stability extends up to 500 °C with minimal mass loss of the biochar support, confirming the suitability of these composites for long-term applications.

Benchmarking against reported biochar-based PCM composites

A comparison of the encapsulation efficiency of the present CBC composites with previously reported biochar-based phase change materials is provided in Table 7. The table compiles data from a wide range of biomass feedstocks (e.g., rice husk, corncob, neem seed, banana stem, wood waste) and different PCMs (paraffin, fatty acids, PEG, etc.). The reported encapsulation efficiencies (R%) vary widely, typically between 30% and 65%. For instance, Mandal et al. obtained 50.92% for neem seed biochar/lauric acid¹⁷, Jeon et al. reported 50.1% for rice husk biochar/palm wax¹⁰¹, and Atinafu et al. achieved 67.98% for food waste biochar/dodecane¹⁰². The present CBC 10 composite, with an R% of 68.25% and an E% of 68.58%, ranks among the highest values reported for unmodified (non-functionalized) biochar supports. This superior performance is attributed to the combination of high accessible pore volume, appropriate pore size (~ 2.1 nm), and the robust carbon framework of the 1000 °C coconut shell biochar. Moreover, the absence of chemical activation residues (confirmed by EDS and XRD) ensures that the capric acid remains pure and no catalytic degradation occurs during thermal cycling.

The crystallization temperatures of the composites (22.75–24.49 °C) are close to that of pure CA (24.25 °C), indicating good heat release behavior. The slight variations are within experimental error and do not affect the practical applicability. The high enthalpy retention after repeated cycles (discussed in section “[Thermal cycling stability](#)”) further confirms the mechanical and thermal stability of the shape-stabilized composites. The observed efficiencies are among the highest reported for unmodified, waste-derived biochar supports. The value of 68.25% for CBC 10 demonstrates that coconut shell biochar pyrolyzed at 1000 °C is a highly competitive support for capric acid, offering a sustainable and cost-effective alternative to synthetic porous carbons.

Leakage resistance, thermal cycling stability, and photothermal response

The practical deployment of shape-stabilized phase change materials (SSPCMs) demands not only a high latent heat storage capacity but also the ability to retain the molten PCM without macroscopic leakage and to withstand prolonged thermal cycling without performance degradation^{23,100}. This section evaluates the leakage resistance of the CBC composites, their long-term thermal reliability over 500 consecutive melt-freeze cycles, and their dynamic thermal response under controlled heating and cooling conditions using infrared thermography.

Leakage resistance

A visual leakage test was performed on pure CA and the four CBC composites by placing 0.5 g of each sample on Whatman filter paper and heating at 55 °C (approximately 20 °C above the melting point of capric acid) for 1

Table 7 Compilation of encapsulation efficiencies and phase change enthalpies for biochar-based PCM composites reported in the literature.

No.	Biochar	PCM	PCM: biochar	ΔH_m (J/g)	ΔH_s (J/g)	ΔH_m (J/g)	ΔH_s (J/g)	R%	E%	Ref.
				PCM		Composite PCM				
1.	Date seed	Capric acid	3:1	164.7	164.5	72.4	71.76	43.96	43.79	81
2.	Orange peel	Myristic acid	4:1	169.7	168.46	67.2	65.14	39.6	39.13	96
3.	Corn cob	Hexadecane	2:1	251.1	249.6	60.2	58.6	24	23.7	51
4.	Wheat straw	Eicosane	2:1	202.2	203	75	75.8	37.1	-	95
5.	Sugarcane bagasse	Organic PCM(OM35)	-	-	-	-	-	53	-	103
6.	Water hyacinth	Organic PCM(OM35)	-	-	-	-	-	30	-	103
7.	Yellow oleander	Organic PCM(OM35)	-	-	-	-	-	39	-	103
8.	Food waste+ wood waste	Dodecane	-	150.4	150.7	102.2	-	67.98	-	102
9.	Rice husk	Palm wax	2:1	-	-	92.13	77.62	50.1	-	101
10.	Oilseed rape	1-Dodecanol	2:1	191.6	-	73.6	-	38.40	-	104
11.	Oilseed rape	n-Dodecane	2:1	150.4	-	90.5	-	60.20	-	104
12.	Miscanthus straw	1-Dodecanol	2:1	191.6	-	62.7	-	62.70	-	104
13.	Miscanthus straw	n-Dodecane	2:1	150.4	-	57.6	-	38.30	-	104
14.	Sewage sludge feedstock	1-Dodecanol	2:1	191.6	-	56.2	-	29.30	-	104
15.	Sewage sludge feedstock	n-Dodecane	2:1	150.4	-	54.1	-	36	-	104
16.	Bamboo	n-Dodecane	-	181.6	-	93.2	-	48.67	-	105
17.	Walnut shell	Methylene palmitate	-	255.46	252.56	138.12	136.61	54.06	-	6
18.	Neem seed	Lauric acid	2:1	186.41	185.76	94.92	92.16	50.92	-	17
19.	Banana stem biochar	Paraffin wax		187.9 ± 2.6	186.9 ± 2.4	128 ± 2.1	128 ± 2.0	-	-	106
20.	Wheat husk	Polyethylene glycol	99:1	142.3	142.5	152.9	146.8	-	-	107
21.	Coconut shell + MWCNT	RT-50	-	192	190	201	197	-	-	108
22.	Wheat straw	RT28	-	228.6	-	51.6	-	22.6	25	109
23.	Softwood	RT28	-	228.6	-	132.3	-	58	61.4	109
24.	<i>Metasequoia glyptostroboides</i>	PEG4000	4:1	190.97	173.98	152.80	123.80	-	-	26
25.	ZnCl ₂ -modified <i>metasequoia glyptostroboides</i>	PEG4000	4:1	190.97	173.98	152.80	133.61	-	-	26
26.	Bamboo	Paraffin wax	-	141.36	141.86	103.69	102.96	-	-	110
27.	Bamboo + graphene	Paraffin wax	-	141.36	141.86	109.96	108.25	-	-	110
28.	Coconut shell	A46	-	158.6 ± 2.21	155.7 ± 2.53	-	-	-	-	111
29.	Coconut shell	A46 + Ag	-	167.6 ± 2.15	164.3 ± 2.31	177.4 ± 2.43	175.8 ± 2.26	-	-	111
30.	Waste pine sawdust	Myristic acid	-	210.7	215.7	138.0	137.8	-	-	112
31.	Poplar saw dust	Stearic acid	-	187.5	186.1	100	96.8	-	-	113
32.	sugar beet pulp	Capric+stearic acid	70wt P	175	168	117	113	-	-	114
33.	Spent coffee grounds	Beeswax	-	43.47	173.6	50.77	43.48	-	-	115
34.	Spent coffee grounds	Palmwax	-	61.12	178.1	76.39	70.71	-	-	115
35.	Spent coffee grounds	Golden soywax	-	-	-	21.05	5.38	-	-	115
36.	Spent coffee grounds	Nature soywax	-	51.81	127.2	19.43	8.54	-	-	115
37.	Terminalia catappa	Polyethylene glycol 400	1:9	97.80	102.75	26.53	28.25	-	-	116
38.	Pinecone	Palmitic acid	6:4	219.63	213.91	84.74	83.81	-	-	28
39.	Apricot kernel shell	n-Eicosan+ Carbon nanofibers	4:1	237.20	236.80	189.20	189.00	-	-	117
40.	Apricot kernel shell	Capric+ Myristic	75wt	170.0	166	125.2	123.1	-	-	118
41.	Apricot kernel shell	lauryl alcohol	75wt	260.1	256.3	193.7	190.7	-	-	118
42.	Apricot kernel shell	n-octadecane	75wt	248	250.4	184.7	184.9	-	-	118
43.	Apricot kernel shell	PEG1000	70wt	160.0	162.0	110.6	112.5	-	-	118
44.	Peanut shell	Stearic acid		187.5 ± 0.7	186.1 ± 1.0	70.6 ± 0.8	67.0 ± 0.9	-	-	119

Table 7 (continued)

No.	Biochar	PCM	PCM: biochar	ΔH_m (J/g)	ΔH_s (J/g)	ΔH_m (J/g)	ΔH_s (J/g)	R%	E%	Ref.
				PCM		Composite PCM				
45.	Waste tire	dodecyl alcohol	78wt	234.2 ± 1.3	233.6 ± 1.1	181.6 ± 1.2	180.2 ± 1.1	-	-	120
46.	Spruce wood	dodecane	-	150.4	-	77.2	-	50.1	51.3	121
47.	Spruce wood	tetradecane	-	194.3	-	67.9	-	37.2	35	121
48.	Spruce wood	octadecane	-	187.9	-	91.5	-	48.7	48.7	121
49.	Garlic peel	OM35	-	156.8	-	121.9	-	77.7	77.96	122
50.	Lemon peel	heptadecane	-	219.1	-	141.8	-	-	-	123
51.	abandoned rice	palmitic-lauric acid	-	171.8	160.5	135.4	124.8	78.8	78.3	124
52.	Longan shell	RT44HC	-	253.2	252.9	264.5	264.1	-	-	125
53.	Phoenix leaves	Paraffin	-	225.24	227.13	148.16	149.49	-	65.80 ± 0.10	25
54.	Phoenix leaves	Stearic acid	-	231.87	231.98	169.30	169.45	-	73.03 ± 0.11	25
55.	Phoenix leaves	PEG	-	188.79	182.85	139.96	137.12	-	74.56 ± 0.12	25
56.	Coconut shell	Capric acid	-	165.42	166.34	112.88	114.61	68.25	68.58	This work

h. Pure CA completely melted and spread into the filter paper, leaving a visible oil stain. In contrast, no stain or wetting was observed on the filter papers for any of the CBC composites. This confirms that the biochar matrices effectively confine the molten capric acid through capillary forces, surface tension and physical adsorption even at temperatures well above the melting point^{17,100}. Although all four composites exhibit sufficient shape stability to prevent gross leakage, the quantitative differences in the actual capric acid content that participates in the phase transition are reflected in their encapsulation efficiencies (Sect. 3.6.1). The absence of leakage for CBC 8.5 is particularly noteworthy given its constricted pore architecture (low BJH adsorption volume, Table 2), indicating that even partially accessible pores provide sufficient capillary retention to immobilize the liquid PCM at the macroscopic scale^{51,126}.

The capric acid retained after the removal step is not surface-adhering liquid but the fraction held within the pore network by capillary condensation. For a wetting liquid the retaining pressure is $\Delta P = 2\gamma \cos\theta/r$; with $\gamma \approx 26 \text{ mN m}^{-1}$ for molten capric acid at 50 °C, complete wetting of the carbon surface ($\theta \approx 0^\circ$) and a pore radius of 1.05 nm derived from the measured mean pore diameter, $\Delta P \approx 50 \text{ MPa}$. This exceeds the 0.1 MPa vacuum applied during the removal step by more than two orders of magnitude, so the filter-paper and vacuum treatments remove the free liquid wetting the external particle surfaces while leaving the confined fraction intact. The confinement is purely physical, as confirmed by the absence of any band shift in the composite FTIR spectra, and is therefore fully reversible. Its principal benefits are leak-free operation without an encapsulating shell and intimate contact between the PCM and the conducting carbon walls. Its costs are equally clear: a thin non-freezing interfacial layer contributes mass without latent heat, confinement in pores of approximately 2 nm broadens and shifts the transition through the Gibbs–Thomson effect, and the loading is capped by the accessible pore volume rather than by the quantity of PCM offered, so that the biochar fraction acts as thermally inert ballast that lowers the energy density relative to the neat acid.

Thermal cycling stability

The long-term reliability of the best-performing composite, CBC 10, was evaluated by subjecting it to 500 consecutive melting-solidification cycles in a DSC instrument. Figure 10a presents the DSC heating and cooling curves of CBC 10 for the 1st and every 50th cycle up to the 500th cycle. All curves overlap almost perfectly with no discernible shift in the peak positions or change in the peak shape, indicating that the phase transition behavior remains stable over the entire cycling protocol^{23,127}. The small variations in the absolute enthalpies are quantified

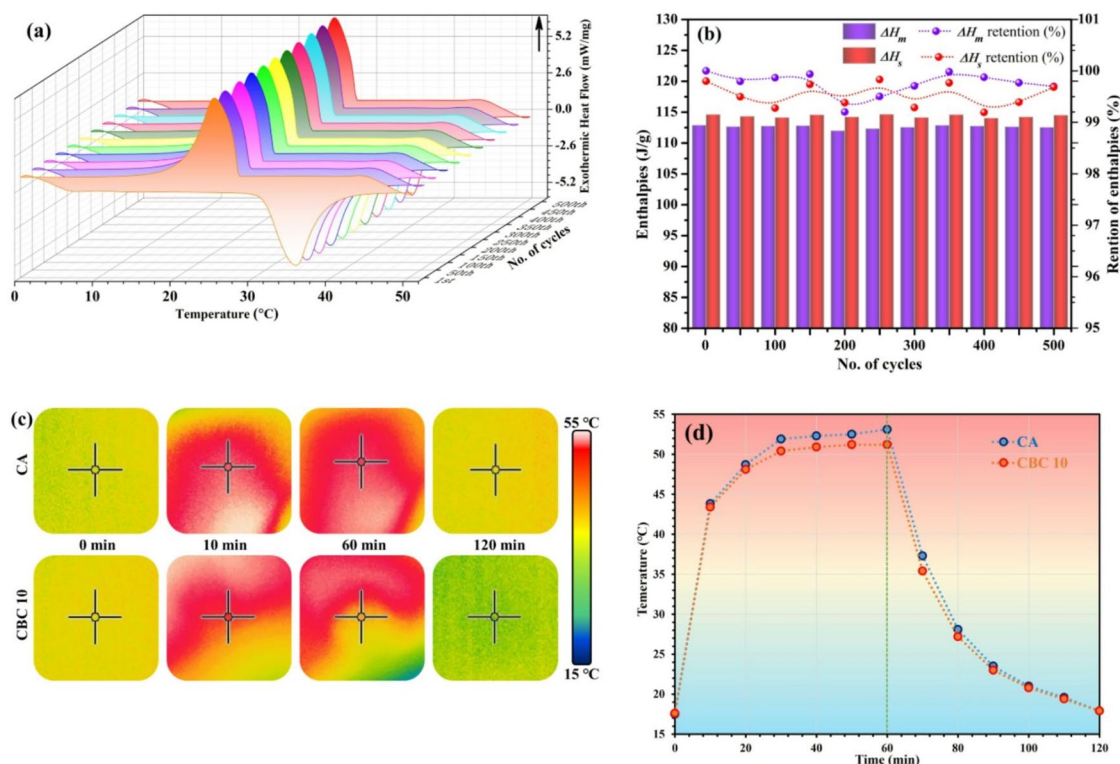


Fig. 10 (a) DSC heating and cooling curves of CBC 10 for the 1st and every 50th cycle up to 500 cycles, (b) enthalpy retention (ΔH_m and ΔH_s) over 500 thermal cycles, (c) infrared thermal images of pure capric acid and CBC 10 at 10 min intervals during heating (15 °C to 55 °C) and cooling (55 °C to 15 °C), (d) temperature-time profiles extracted from the thermal images.

in Fig. 10b, which plots the retention of melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_s) relative to the values of the 1st cycle. The melting enthalpy decreased from 112.88 J g⁻¹ (1st cycle) to 112.00 J g⁻¹ (500th cycle), a reduction of only 0.8%. The crystallization enthalpy decreased from 114.61 J g⁻¹ to 114.02 J g⁻¹, a reduction of 0.5%. Both values lie well within the typical experimental error of DSC measurements ($\pm 2\%$), demonstrating that CBC 10 retains its thermal energy storage capacity over prolonged use. Similar high cycling retentions ($\geq 95\%$ after 200–1000 cycles) have been reported for other biochar-based PCM composites, confirming the excellent durability of this class of materials^{29,109}.

The outstanding cycling stability of CBC 10 is attributed to the absence of chemical degradation due to the purely physical interaction between capric acid and the biochar, the rigid and thermally stable carbon framework of the 1000 °C biochar, and the complete removal of residual ZnCl₂ (confirmed by EDS and XRD), which could otherwise catalyze undesirable side reactions^{26,51}.

Dynamic thermal response

The heat absorption and release behavior of pure CA and CBC 10 was visualized using an infrared thermal imaging camera during heating from room temperature to 55 °C and subsequent cooling to room temperature (1 h each). Figure 10c presents infrared thermograms of the two samples at selected intervals during heating and cooling, while Fig. 10d shows the corresponding temperature-time profiles extracted from the geometric centre of each sample.

During the heating phase, pure CA rapidly increases in temperature and reaches 55 °C within approximately 25 min, after which the temperature continues to rise slightly above the set point due to the absence of a phase

change thermal buffer. In contrast, CBC 10 exhibits a slower temperature rise with a noticeable reduction in the heating rate between approximately 35 °C and 37 °C, corresponding to the melting range of capric acid (Table 6). This inflection is a direct signature of latent heat absorption: as the PCM melts, it absorbs thermal energy without an equivalent temperature increase, thereby providing a thermal buffering effect. Once the PCM is fully melted, the temperature of CBC 10 rises more quickly but remains below that of pure CA at equivalent heating times, confirming effective thermal regulation^{17,51}. During the cooling phase, pure CA cools down rapidly, with no evidence of a recrystallisation plateau in the temperature trace. CBC 10, however, exhibits a pronounced recrystallisation plateau near 24 °C, where the temperature remains nearly constant while the solidification exotherm is released. The cooling rate is noticeably slower for CBC 10, and the overall temperature drop is more gradual, indicating that the stored latent heat is released over an extended period. The appearance of a distinct plateau during cooling further confirms that the capric acid remains fully functional within the biochar matrix and can undergo reversible phase transitions^{17,51}.

The ability of CBC 10 to absorb heat at a near-constant temperature during melting and release it during solidification directly translates into reduced temperature fluctuations and improved indoor thermal comfort when integrated into building envelopes. The dynamic thermal response, together with the leakage resistance and excellent cycling stability documented in sections “[Leakage resistance](#)” and “[Thermal cycling stability](#)”, demonstrates that coconut shell biochar pyrolyzed at 1000 °C produces a shape-stabilized PCM that is exceptionally well-suited for passive building thermal management applications^{9,26,100}.

The three properties examined in this section respond to pyrolysis temperature in different ways. Leakage resistance is essentially independent of it, because the retaining capillary pressure scales inversely with pore radius and the mean pore diameter varies only from 2.05 to 2.25 nm across the four supports, so that every composite develops a retaining pressure of order 50 MPa. Pyrolysis temperature governs how much capric acid is taken up, not whether the retained fraction escapes, which is why CBC 8.5 is leak-free despite its constricted pore entrances. Cycling stability, by contrast, improves with pyrolysis temperature: the interlayer spacing falls from 0.346 to 0.370 nm at 850 °C to 0.336 nm at 1000 °C and the stacking coherence length rises from approximately 1.0 nm to 1.9–3.2 nm (Table 3, section “[Nanoscale pore-wall architecture by HRTEM and SAED](#)”), so that pore walls of six to ten coherently stacked layers withstand the repeated dimensional change of the melting PCM far better than walls of three curved layers, while the fall in surface oxygen from 15.73 to 3.52 mass% reduces the sites available for esterification or oxidative side reactions with the carboxylic acid. The dynamic thermal response scales most directly of all, since the amplitude and duration of the buffering plateau are set by the stored latent heat, which rises from 69.92 to 112.88 J g^{−1} across the series, while the increasing structural order raises the thermal conductance of the framework and sharpens the onset of the plateau.

Sustainability assessment

To contextualize the environmental merit of the 1000 °C coconut shell biochar relative to conventional PCM supports, a simplified carbon balance was performed using published embodied carbon values. Based on the measured biochar yield of 23.7 wt% and the carbon content of 74.18 mass% (Table 1), values consistent with those reported for ZnCl₂-activated lignocellulosic feedstocks¹²⁸, pyrolysis of waste coconut shell sequesters approximately 0.645 kg CO₂-eq kg^{−1} of feedstock processed, calculated following the carbon sequestration accounting methodology of Lehmann et al.¹²⁹. Since the carbon content is derived from energy-dispersive spectroscopy, which samples the near-surface region and does not determine light elements quantitatively (Sect. 3.1), this figure should be read as an indicative estimate rather than a bulk determination, and the comparisons that follow rest on the substitution of one support material for another rather than on its absolute value. For a composite containing 31.75 wt% biochar support, replacing expanded graphite (embodied carbon ≈ 1.8 kg CO₂-eq kg^{−1}) avoids approximately 0.571 kg CO₂-eq kg^{−1} of composite produced, while replacing coal-based synthetic activated carbon (embodied carbon ≈ 3.5 kg CO₂-eq kg^{−1}) avoids approximately 1.11 kg CO₂-eq kg^{−1}. A direct life cycle comparison confirms that biochar consistently outperforms synthetic activated carbon across environmental

impact categories¹³⁰. The additional energy cost of pyrolysis at 1000 °C relative to 850 °C corresponds to only approximately 0.014 kg CO₂-eq per 300 g batch at the Korean grid carbon intensity of 0.459 kg CO₂-eq kWh⁻¹¹³¹, which is negligible in comparison. These estimates confirm that the use of waste-derived coconut shell biochar as a PCM support is not only technically competitive but carries a substantially lower carbon footprint than fossil-derived alternatives, consistent with circular economy and carbon neutrality objectives.

Conclusions

This study demonstrates that the pyrolysis temperature of coconut shell biochar critically governs the accessible pore volume and, consequently, the thermal energy storage efficiency of capric acid based shape-stabilized phase change composites. The biochar pyrolyzed at 1000 °C achieves the highest encapsulation efficiency of 68.25%, which is among the best reported for unmodified waste-derived biochar supports. The key findings are summarized below.

- (i) Increasing the pyrolysis temperature from 550 °C to 1000 °C progressively raises the BET surface area (from 482 to 759 m² g⁻¹) and, between 850 and 1000 °C, the accessible pore volume (BJH adsorption volume from 0.110 to 0.130 cm³ g⁻¹), directly correlating with higher capric acid loading.
- (ii) The pore structure evolution schematically illustrated in Fig. 4 and supported by N₂ sorption analysis reveals that the biochar pyrolyzed at 850 °C develops constricted pore entrances (total pore volume 0.376 cm³ g⁻¹ but BJH adsorption only 0.110 cm³ g⁻¹), yet its encapsulation efficiency (57.59%) still exceeds that of the 700 °C sample (50.57%), indicating that total pore volume also contributes to PCM retention when accessible volume is limited. High-resolution electron microscopy shows that the pore walls of the 850 °C biochar consist of short, strongly curved graphene fringes that close upon themselves, whereas those of the 1000 °C biochar form extended parallel stacks bounding open channels (section “[Nanoscale pore-wall architecture by HRTEM and SAED](#)”).
- (iii) The shape-stabilized composite CBC 10 shows a melting enthalpy of 112.9 J g⁻¹ and an encapsulation efficiency of 68.25%, with a phase transition temperature (35.6 °C) ideally suited for building thermal management.
- (iv) Thermogravimetric analysis confirms that the actual capric acid content in the composites matches the DSC-derived efficiency values (e.g., 66.4% weight loss for CBC 10 versus 68.25% efficiency), validating the reliability of the latent heat measurements.
- (v) All CBC composites are completely leak-proof at 55 °C, with no visible staining on filter paper after 1 h, confirming effective confinement of molten capric acid by the biochar matrix.
- (vi) CBC 10 retains more than 99% of its melting and crystallization enthalpies after 500 consecutive thermal cycles, demonstrating excellent long-term thermal reliability.
- (vii) Infrared thermal imaging reveals that CBC 10 exhibits a slower heating rate with a clear inflection near the melting point (35–37 °C) and a pronounced recrystallisation plateau near 24 °C, confirming effective thermal buffering and heat regulation.
- (viii) The 1000 °C coconut shell biochar is a sustainable, cost-effective and high-performance support for capric acid, offering a competitive alternative to synthetic porous carbons for passive building energy conservation.
- (ix) The phase transition temperatures of CBC 10 (melting at 35.6 °C, crystallization at 24.5 °C) lie within the typical human comfort range for buildings, enabling passive regulation of indoor temperature fluctuations and reducing heating and cooling energy demand.

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Data availability The datasets used or analyzed during the current study are available from the corresponding author upon reasonable request.

Competing interests The authors declare no competing interests.

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