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Solar Energy Materials and Solar Cells



Leakage-free porous cellulose-based phase change cryogels for sound and thermal insulation

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ABSTRACT

Leakage-free phase change materials (PCM) are used as passive energy storage systems that thermoregulate indoor environments. In this research, we synthesized highly porous hybrid materials based on non-covalent physical interactions between (poly)ethylene glycol (PEG) and modified cellulose nanofibrils (CNF), namely lignin-containing CNF (LCNF) or acetylated CNF (ACNF). The PEG/CNF hybrid, termed phase change nano-hybrids (PCN), were ultra-lightweight (0.022–0.043 g/cm³), mechanically resilient, and displayed a high latent energy storage, up to 204 J/g. The PCN systems (specific heat capacity as high as 2.24 J/g K) were effective in thermal regulating 2.23 °C with a 1 mm thickness coverage while maintaining thermal stability. The PCN also demonstrated favorable thermal management under excess solar heating, providing 33.5 °C of insulative protection with a 1.5 cm thick system. The PCNs have exceptional acoustic absorbance (100% absorbance for 1600 Hz and 50% at lower frequencies, 500 Hz). Trace metal oxide (TiO₂) nanoparticles improved the PCN thermoregulating abilities, revealing desirable opportunities in multi-functional applications. Our biobased PCN is a promising insulation and passive energy storage alternative for thermal protection in smart building, electronic, packaging, energy storage system and aerospace sectors.

1. Introduction

Global carbon dioxide (CO₂) emissions are reaching critical levels and their environmental impacts are projected to rise with population growth [1]. A significant contributor of CO₂ emissions (30%) comes from building heating and cooling, accounting for 10% of the global energy consumption [2]. Building insulations reduce the energy waste involved with indoor cooling and heating processes. However, traditional insulators are sourced from non-renewable, petrochemical-based polymers such as polystyrene. For most polymer materials, their end-of-life leads to the accumulation of non-degradable components that lead to toxic terrestrial and oceanic leakage [3,4]. Another significant contributor of CO₂ emissions arises from the transportation of heavy building materials; thus, designing an efficient, ultra-lightweight insulator relieves transportation related emissions [5,6]. A focus should be placed in improving energy efficiency, as emphasized by the European Union's SDG 7a [7]. Thus, innovative, thermoregulating biodegradable materials are valuable options to improve energy conservation.

Mineral wool, natural fibers, and cellulose are some of the available biobased and thermally insulating materials [8]. Although they are derived from minerals, animals, or plants, some disadvantages exist. For instance, although mineral wool has low thermal conductivity (0.024 W/m K), it is heavy (70 kg/m³) for handling and transportation [9]. Natural fibers derived from coconut or wool are challenging to mass produce, as the amount of biomass and agricultural resources required to make the material is costly; thus, the number of resources needed to produce these materials may not offset their overall advantages. Cellulose fiber (derived from raw or recycled paper or wood stocks) is used as filler injected into cavity frames for construction [10] but is less resilient to mechanical and water loading stress compared to non-biomaterial insulators [11,12]. Therefore, conceptualizing a renewable-based biomaterial with ecologically and energetically feasible uses remains as an unmet objective.

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Phase change materials (PCMs) can be applied to indoor spaces to thermoregulate local environments, conserve energy waste, and store excess latent heat that is otherwise not utilized [12,13]. In principle, PCMs thermoregulate when temperature fluctuations occur. During crystallization, latent heat is released; conversely, during heating, excess heat is absorbed to maintain a steady, cooler temperature. PCMs that are currently commercialized as "smart" building materials, like paraffin wax, has a high specific heat capacity (2.8 J/g K) and latent energy storage (170–270 J/g) [14]. However, a main issue that is being addressed herein is the leakage of PCMs after fusion that limits their handling and application in products [15].

The PCM used in this study is (poly)ethylene glycol (PEG) which can act as a great thermal regulator due to its tunable fusion enthalpy and temperature (35-60 °C), depending on its molecular mass [16]. This makes PEG interesting for different thermal applications. PEG possesses biodegradable, bio-compatible, non-toxic, non-corrosive and competitive price properties. It can also be derived from renewable bio-based sources [17]. As demand for sustainability increases and the oil industry becomes more obsolete with climate action policy agendas, biodegradable and renewably sourced products are in high demand. Analogous to the other liquid-to-solid PCMs, a disadvantage of PEG is however its leakage and fluidity during melting. Porous carbon has been commonly used to address leakage issue of PEG [18-22]. PEG also shows a high compatibility with other biopolymers, such as cellulose, which can be a solution towards a leakage-free thermal performance. This can also alleviate the shrinkage or expansion of the PCM over continuous heating-cooling cycles [23].

Emulsification of paraffinic PCMs with cellulose nanofibril (CNF) was reported to address the leakage issue [24,25]. Herein, CNF is our preferred material not only to prevent the leakage issue of PEG, due to their highly compatible nature [16,26], but also to enable high porosity which is an important characteristic for insulation. Heat transfer can be decreased through the alteration of the material's porous structure [27]. Heat transfer mechanisms in high porosity materials involve convection, radiation, gas conduction and solid conduction [28,29]. Gas conduction is a main contributor to heat transfer in highly porous materials such as foams or aerogels. In theory, the Knudsen effect and phonon scattering phenomena improves insulation when the pore structure's mean free path is smaller than the gas molecules. Nanocellulose fibers have the advantage of forming smaller pore sizes in hybrid materials compared to non-microfibrillated cellulose [30]. By controlling the material's porosity and dimension, induced phonon scattering effect and interfacial roughness can affect thermal conduction [27,28].

The PEG and CNF hybrid material is herein referred to as a phase change nanohybrid (PCN) and can be classified under organic glycol PCMs [16]. PCM and insulation can be used for thermal regulation and protection purposes. While PEG regulates temperature by its energy absorbance ability through phase change, insulation prevents heat transfer by its highly porous structure and low thermal conductivity. PCN solution combines these two functions in one material that have the porous structure of an insulation and phase change ability of a PCM with no leakage or volume change of the melt phase. The porous structure is a result of the cellulosic scaffold together with appropriate processing method and latent heat storage comes from the PCM content. High loading of PEG (85% dry weight) incorporated into a CNF matrix via PEGylation of non-covalent interactions create a solid formation at room temperature that becomes an organogel above its melting point. This solid-gel phase change is what relieves PCM leaking past its melting temperature, illustrated in Fig. 1.

We previously reported form-stabilization of PEG with a TEMPOoxidized nanocellulose (TEMPO-CNF) matrix that demonstrated high thermally insulating properties (0.040 W/m K), high mechanical strength as a film (tensile strength was 28 MPa), and ultra-lightweight, attributed to CNF's high porosity and low density (1.6 g/cm^3) [16]. Modification of nanocellulose can provide numerous physical interactions as superabsorbent of liquids [31]. We hypothesize that different processing techniques and incorporation of additives can tailor the surface chemistry and porosity, ultimately affecting the thermal properties for better insulation. As such, this study focuses on a material that is comprised of PEG, titanium dioxide (TiO2) and modified CNF which successfully prevents phase transition leakage and provides exceptional porous structure with low thermal conductivity. Further exploration of modified CNF scaffolds is considered to improve PCN properties through variable processing methods. Such product is an excellent alternative for commercial insulation material such as polystyrene that are fossil-fuel-based with big carbon footprint. Ideal qualities were focused on the form stability and texture of the sample (low hardness, low brittleness, and increased apparent elasticity), porosity (micro to meso pore distribution), and thermal properties (latent heat storage, specific heat capacity, heat transfer and thermal conductivity). Morphological characterizations were studied with scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) and dynamic mechanical analysis (DMA). Thermal and acoustic properties were measured with differential scanning calorimetry (DSC), infrared (IR) thermal camera, thermal conductivity analyzer and acoustic impedance tube.



Fig. 1. Form-stability and leakage-proof phase transition of a phase change nanohybrid (PCN-L3) composed of PEG (74 wt%), lignin-CNF (24 wt%) and TiO₂ (2 wt%) through intermolecular interactions and hydrogen bonding.

2. Material and methods

2.1. CNF modification

Cellulose nanofibrils (CNF) were produced from never dried and partially delignified (2.7% residual lignin) birch pulp fibers that were subjected to bleaching and mechanical grinding. The CNF was modified by heterogeneous acetylation (ACNF), as previously reported [32]. The method reported by Imani et al. [33] was used to prepare lignin-containing nanofibril (LCNF) suspensions (1.131% wt) from unbleached spruce and pine softwood recycled fibers.

2.2. PCN preparation

Phase change nanohybrids (PCN) were formulated with various concentrations of ACNF or LCNF suspension (0.5–1.0% by dry matter content) and (poly)ethylene glycol (PEG, Sigma- Aldrich, Mw 4000). PEG was dissolved in Di-H₂O at < 50 °C, then mixed with CNF aqueous suspension under mechanical stirring (~1 h), resulting in sample concentrations that ranged from a ratio of 85-60% PEG to 15–40% modified CNF by dry weight.

The suspensions were then processed via three different processing methods, as illustrated in Fig. 2. 3D bio-printed samples were produced with a BIO X 3D bioprinter (CELLINK, Gothenburg, Sweden), using a pneumatic 0.63 mm gauge tip, under 8-14 mm/s and 25-60 kPa to produce 27 mm \times 5 mm grid-lattice patterned pellets. Pellets were prefrozen (24 h), then freeze dried (Labconco Freezone 2.5). The freeze templating samples were poured into graduated polypropylene centrifuge tubes and centrifuged (3 min, 3500 rpm). PCN mixtures were manually immersed in liquid nitrogen (1 mm/min), then immediately freeze dried (72 h). Casted samples were poured into 60 mL polypropylene lab grade containers for pre-freezing (24 h), then freeze dried (48 h). All samples were stored at room temperature. Titanium (IV) oxide anatase (Sigma-Aldrich, 2% dry wt) was dispersed and ultrasonicated in distilled water, added to the PCN suspension, homogenized until full dispersion and then frozen and freeze dried. Table 1 is a compilation of the developed compositions.

PEG N

CNF

Fable 1		
Naming and	composition	of PCNs.

Sample	Dry matter of CNF	Composition of PCN						
	suspension (% dry wt)	Modified CNF (% dry wt)	PEG (% dry wt)	Additive (TiO ₂) (% dry wt)				
Acetylate	d CNF (ACNF)							
PCN-	0.85	15	85	0				
A1								
PCN-	0.92	20	80	0				
A2	0.50	05		0				
PCN-	0.50	25	75	0				
A3 PCN-	0.50	24	74	2				
A4	0.00	27	74	2				
PCN-	0.47	40	60	0				
A5								
CNF-	0.92	100	0	0				
A0								
Lignin-co	ntaining CNF (LCNF)							
PCN-	1.13	20	80	0				
L1								
PCN-	0.50	25	75	0				
L2	0.50		- 4	0				
PCN-	0.50	24	74	2				
L3 DCN	1.00	24	74	2				
L4	1.00	27	/ 7	2				
CNF-	1.13	100	0	0				
LO	· · ·		-	-				

2.3. Material characterization

Scanning electron microscopy. The cross-sections of PCN microstructures were observed with scanning electron microscopy (SEM, Zeiss Sigma VP, Germany). SEM was operated under vacuum, using a voltage range of 2–4 kV. Dried PCN samples were sputter coated (LECIA EM ACE600 sputter coater) with 4–6 nm of gold or gold-palladium alloy prior to imaging. Carbon tape was used to fix the samples on to metal stubs.

Pore Distribution. BET Analyzer (Mimetrics Tristar II 3020) with isothermal (77.4 K) nitrogen adsorption of dried samples (15.8–51.6



Additives 🔎

Fig. 2. Schematic of PCN processing variations: 3D Printing, Freeze Templating, and Casting.

mg) were measured at relative pressures and degassed with nitrogen (FlowPrep 060) at 50 °C for approximately 2 h, prior. Barrett-Joyner-Halenda (BJH) method was used to report pore volume distribution in the range of 1.7–300 nm diameter pores, and to observe incremental pore volume (2–40 nm). Porosity was determined (equation (1)); the ratio of air volume to the cryogel total volume.

$$f = 1 - \frac{\rho}{\rho_0} \tag{eq. 1}$$

where f indicates the cryogel porosity, ρ indicates the crogel apparent density, and ρ_o indicates the PCN's density [34] with respect to the calculated bulk density.

Dynamic mechanical analysis. Change in volume by compression impact was reported using dynamic mechanical analysis (DMA Q800, TA Instruments). The compression analyzer was programmed to a customized tensile mode where the stress-strain was measured under isothermal conditions (25 °C). The ramp loading rate was set to 1 N per minute of up to 6 N to 16 N compressive force. All samples were prepared as pellets, ~10 mm in height and ~30 mm in diameter. Strain percent and static force were determined with TA universal analysis software.

Acoustic (Impedance). Sound absorbance was determined with ISO 10534:2 Impedance tube transfer function method. The signal processing system consisted of an amplifier with a two-channel Fast Fourier Transform (FFT) analyzing system. Impedance testing was measured in the range of 50–6000 Hz. Samples were shaped to fit a 29 mm diameter impedance tube, each having the thickness of 30 mm, except for sole CNF (25 mm). Commercial mineral wool was measured as a reference. Table S1 provides samples composition and dimensions for the acoustic measurement.

2.4. Thermal measurements

Differential scanning calorimetry (DSC) was used to measure fusion temperature, enthalpy and specific heat capacity with a NETZSH DSC204F1 Phoenix device. Samples were prepared in aluminum crucibles, \sim 5 mg each. A dynamic heat flow program was set from -20 to 80 °C. Initially set at room temperature, a 5 K/min heating rate was installed for four cycles. The specific heat capacity was evaluated using sapphire as standardization. All measurements were repeated at least

three times on three different replicates of each composition. Thermal stabilization was demonstrated with cyclability (100 consecutive cycles). A TCi Thermal Conductivity Analyzer (C-Therm) using modified transient plane source (MTPS) technique was implemented to determine thermal conduction measurements (see Fig. S1 in the Supplementary Information). The sample was subjected to 1–3 s pulses of current, and the induced voltage drop was recorded as the inverse proportionality of the voltage rate to indicate thermal transfer. The samples were shaped as 29 mm diameter pellets.

2.5. Insulation performance

To simulate a small model house, a wooden box was insulated by enclosing it with 0.5-cm thick insulation material. The model was centered between two studio lamps (2000 W Halogen optic lamp, Osram) 40 cm away at 45° angles (Fig. 3). Thermocouples were fixed to the samples to measure interior and exterior temperatures. Structural deformation, physical stability, and phase changes were observed under irradiation, using a mid-wavelength (MWIR) infrared camera (FLIR SC7600) with Research IR Max program. Each sample was heated under irradiation (10 min) and cooled "off-irradiation" (30 min). The average light intensity was 500 W m⁻².

3. Results and discussion

3.1. The effect of processing method

PCN samples were composed of two different nanocelluloses (ACNF and LCNF) and various composition ratios. The ratio of PEG to CNF (dry weight basis), ranged from 85:15 to 60:40, respectively, as compiled in Table 1. Fig. 4 and Fig. S2 show the images of the samples produced via different processing methods. The brownish color of compositions containing LCNF originates from its residual lignin content.

The freeze templating method was used to induce anisotropy within the sample's cylindrical structures, where the fibrils are theoretically forced unidirectionally in the radial direction. The technique conformed to the container's cylindrical shape, maintaining the occupied organogel volume. Visual inspection indicated that the pores were oriented in one dominant direction; however, wave patterns were also apparent. Residual water in the structure may cause structural collapse, which can be



Fig. 3. a) Experimental set-up scheme of insulated box demonstration, b) bare wooden box "model house", c) mineral wool insulated wooden box, and d) PCN-L2 insulated wooden box (0.5 cm thick sheets).



Fig. 4. PCN dried samples produced from different processing: 3D bioprinting (a), freeze templating (b) and casting methods (c) based on PCN-L1 composition as well as casted PCN-L3 composition (d).

resolved by longer freeze-drying time. The highest concentration of PEG-to-CNF ratio that displayed form stability was 80:20. Nanocellulose based 3D bioprinting is an emerging technique used to tailor macro-structures with great precision [35]. 3D bioprinting can directly

influence the structure's thermal conduction and absorption by controlling pore interconnectivity. Lightweight efficiency and mechanical strength can be tailored by adjustments of the infill density of a geometrically stable scaffold. The 3D printed scaffolds exhibited



Fig. 5. SEM images revealing different degrees of pore alignment for PCN-A2 3D printed (a), PCN-A2 freeze templated (b), PCN-L1 3D printed (c), PCN-L1 freeze templated (d), PCN-L3 (e) and PCN-L4 (f).

relatively large open macropores (\sim 125 µm, Fig. 5), contributing to a light weight. The casting is a simple method that promoted structural elasticity suitable for insulation application. Casting provided the most desired qualities in the texture of the samples such as low hardness, low brittleness, and increased apparent elasticity. It also resulted in porosity with appropriate micro to mesopore distribution and great thermal properties, which are discussed in the following sections. Fig. S2 in the supplementary information shows the APCN compositions.

3.2. Physical characterization

Morphology. Morphological observations with SEM provided insight for surface and cross-sectional bulk pores. Pore interconnectivity, range of macropore distribution, and open or closed cell configuration was observed. SEM imaging verified the existing degree of pore alignment by freeze templating method in some APCN and LPCN samples (Fig. 5). Visualization of the scaffold filling and assembly within cast samples was also observed, such as, thickness of layers and fibers. Phase segregation did not occur for any of the LPCN samples (not the cast samples). Fig. 5 displays the SEM images of pore alignment induced by freeze templating, and the macro-pore sizes of lignin and acetylated CNF produced scaffolds of the 3D printed PCNs. The PCNs exhibited interconnected, open pore cells. This highly porous cryogels differ from that of previously reported PCM-CNF composites [16,24], which we assume plays a significant role in insulation properties of the PCNs.

Porosity. In accordance with the Knudsen effect, a desirable pores size for insulating material would provide a mean free path that is smaller than that of the gas molecules (50 nm). BJH method can provide an incremental pore size distribution which gives an idea of the dominating mesopore sizes found in each sample (Fig. S3 in the Supplementary Information).

Freeze templated samples showed an increased number of smaller pores. Freeze templated and casted samples formed micro, meso and macro-porous distributions (2-180 nm), suggesting a broad distribution of available pores sizes. Qualitative differential pore volume was reported, since volumetric porosity measurements made by gas adsorption methods can misrepresent cumulative micro and mesoporous volume, accounting for error in experimental point spacing that can enlarge the pore radii represented in the sample [36]. Bulk density and porosity were defined by equation (1). The bulk density for the PCNs ranged from 0.022 to 0.043 g/cm³ and porosity ranged from 95.8 to 98.1%. It was also observed that the dilution of the initial dry matter concentration of CNF stock suspension can lower the density and increase porosity in the final PCN product. The densities corresponded to previous research of cellulose cryogels (0.003-0.200 g/cm³) [37] and increased with PEG content (1.2 g/cm³) and TiO₂ additive content (3.9 g/cm³). The wet impregnation method was previously reported to create limited porosity in cellulosic composites, while freeze-drying formed highly porous structures with oriented channels [38].

Mechanical Strength. Structural resilience is an important property for insulation in buildings and packaging for transport. The PCN was observed under mechanical stress and the strain percent was measured using a programmed DMA strain ramp under compressive force. Strain percent measurements imply an amount of form recovery after relaxation time and sample height measurements. PCN-L3 exhibited 28% strain under 6 N force and was able to recover 82% of its form after 1 min. Consecutively, a 16 N compressive force was exerted and measured a 69% overall strain; after 1 min of relaxation, the PCN showed 43.8% height recovery. Figs. S4 and S5 and Table S2 in the Supplementary Information provide the compression graphs and images.

Sound Absorbance. Sound absorbance alleviates noise pollution in applications, such as building and transport. Acoustic research on CNF is sparse; however, porosity in acoustic absorbers has been well researched. The acoustic alleviation mainly depends on the porous structure and the solid content of the material, while porosity and

density play the main influential roles in sound absorbance. Sound waves passing through highly porous materials experience multiple reflections, refractions, and absorption on the pore walls which can decay or exhaust the sound energy [39]. For instance, lower frequency band absorbance could increase with open pore cell structures with interconnectivity. Polyurethane foams can achieve absorption frequencies as low as 250 Hz, and 100% absorbance with interconnected pores structures compared to closed cell porous structures. Moreover, the open and interconnected pore diameters ranged from 350 to 1050 μ m [34].

The casting method was used to prepare the PCN samples, i.e., PCN-A5 and PCN-L1, for acoustic measurement, since they have structures which are shelf-like scaffolds with open celled interconnected pores. Their pore diameters range from 100 to 500 μ m, congruent to successful acoustic polyurethane foams, mentioned. PCN-A5 and PCN-L1 samples demonstrated notable acoustic absorption; demonstrating up to 100% absorption ratios and were able to absorb low frequencies below 1000 Hz. Sound absorption impedance measurements were conducted for PCN samples in the range of 500–6000 Hz which is the acoustic frequency range conceivable to human ear (Fig. 6). PCN-A5 exhibited 100% absorbance at moderate frequencies (1600 Hz). The PCN-L1 sample reached 90% absorbance ratios at 5000 Hz and exhibited 50% absorbance at lower frequencies (500 Hz). PCN-L1 acoustic absorption behavior resembled coefficients close to that of the commercial mineral wool, achieving absorbance within a low frequency range.

Previous research indicated that CNF and CNC foams that were developed for acoustic panels exhibited low absorption ratios (54–57%, 4000 Hz) and were poor absorbers of low frequencies (<1000 Hz) [40]. This is also confirmed in this research as the reference sample prepared with sole CNF showed poor sound alleviation. However, after the addition of PEG, the performance was enhanced which suggests the positive effect of PEG in the favor of acoustic absorbance. Cotton-based cellulose hydrogels were processed with directional freezing to solve the irregular distribution and coexistence of open and closed pore structures. Cellulose aerogels with regularly distributed and axially open porous structure were developed to enhance the sound-absorbance. The sound absorption coefficient of directional aerogel reached 0.88 at 4500 Hz with 0.055 g/cm³ density and 89% porosity [41]. A sound reduction coefficient up to 0.6 was observed for straw-based aerogels 0.05–0.06 g/cm³ density and 97% porosity [42].

3.3. Thermal properties

Latent Heat Storage. The PCNs demonstrated relatively medium to high heat storage capability, mainly in the range of 100-160 J/g. Neat PEG (Mw 4000) is capable of latent heat storage up to 180 J/g. The PCN-L series produced a consistent range (Fig. 7). The PEG content and processing methods affected the thermal properties (enthalpy and C_p). Moreover, the dry matter content of the CNF suspension also demonstrated to influence the enthalpies. In the case of ACNF suspensions, lower dry matter content measured lower enthalpies.

Specific heat capacity (C_p , J/g K) plays an important role in temperature regulation. Higher C_p values enable the PCN to increase the energy barrier needed to promote phase change; meaning, a larger resistance to phase change gives a higher latent heat storage density and higher sensible heat storage capacity. In regulating indoor temperatures, the storage and release of the isothermal latent energy via melting and crystallization is more efficient for maintaining comfortable environments [43,44].

Fig. S6 in the Supplementary Information shows the C_p graphs of the samples. The C_p for the solid ($C_{p, s}$) and liquid ($C_{p, l}$) phase appeared to be the highest in the casted samples. The PCNs were further modified with trace amounts of additive, to observe changes in passive energy storage of the material. The additive was 2% nanosized TiO₂ by dry weight, giving only slight changes in values for enthalpy and C_p . Heat of fusion values were similar for most PCN samples which measured up to 204 J/g; the average was 138.4 J/g and fluctuated ± 2 °C. Accordingly,



Fig. 6. Sound absorbance coefficients over a frequency of 500–6000 Hz for PCN-A5 and CNF-L1 (embedded images), as well as reference samples made of CNF + PEG (20:80 wt%), sole CNF and mineral wool for comparison.



Fig. 7. DSC curves for (a) heating and (b) cooling cycles under 5K/min scan rate; a comparison of different PCN compositions. Table 2 includes related phase change properties.

Table 2

Thermal	proper	rties of PCNs	based on	the DSC	measurements i	n Fig. 7	. C _Ρ .	and C _P	1 reported a	t 10 and 75	°C, respectivel	v. R (%) i	is PCM loadii	ng efficiency	v.
	F - F -					0	· - F .3	· · · · · ·						0	

Composition	Processing Method	T _m (°C)	ΔH_m (J g ⁻¹)	$\Delta H_c (J g^{-1})$	R (%)	$C_{P,s} (J g^{-1} K^{-1})$	$C_{P,l} (J g^{-1} K^{-1})$
Acetylated CNF	(ACNF)						
PCN-A1	3D Print	57.4	144.1	-138.1	80	1.89	1.58
PCN-A2	3D Print	59.6	135.3	-128.4	75	0.83	1.35
	FT	60.2	150.7	-141.4	84	2.24	3.24
PCN-A3	Cast	56.8	123.6	-118.1	68	1.4	1.9
PCN-A4	Cast	58.4	115.1	-109.7	64	1.16	1.76
PCN-A5	3D Print	63.4	180.3	-171.4	100	1.12	1.59
	FT	60.8	204.1	-195.5	113	2.12	2.7
	Cast	55.2	60.12	-58.54	33	1.34	1.2
Lignin-containin	ng CNF (LCNF)						
PCN-L1	3D Print	58.8	138.5	-133.9	77	1.02	1.42
	FT	58.6	135.5	-131.7	75	1.04	1.40
	Cast	57	159.8	-152.5	89	1.21	1.55
PCN-L2	Cast	57.8	152.4	-148.0	84	1.32	1.78
PCN-L3	Cast	58.2	142.6	-137.2	79	1.27	1.86
PCN-L4	Cast	57.4	142.0	-137.3	79	1.21	1.94

the PCM loading efficiency of the composites was calculated via following equation [45]:

$$R = \frac{\Delta H_{m,PCN}}{\Delta H_{m,PEG}} * 100$$
 (eq. 2)

 $\Delta H_{m,PCN}$ and $\Delta H_{m,PEG}$ are the melting enthalpy of the PCN composition and pristine PEG obtained from DSC, respectively. The R values (Table 2) for compositions PCN-A4 and PCN-A5 made through 3D-printing and freeze-templating, respectively, indicated the highest PCM loading efficiency. This can also be related to a higher degree of crystallinity (X) for the composite versus the sole PCM [45]. Higher X values indicate better preservation of crystallinity, prevention of polymorphs and weaker interactions with the supporting materials. Acetylation reduces the polarity of the fiber surface and relatively weakens the interactions with PCM. Presumably, the acetylated cellulose under freeze-templating or freeze-drying shows significantly lowered surface polarity interactions with PCM, which facilitates crystallization. The two mentioned samples also showed a rigid and brittle physical structure compared 6 to the rest of the compositions (as seen in Fig. S8), which can be signs of alteration in intermolecular interactions and inapplicability for the target purpose. The DSC graphs of this sample (Fig. S8) showed two distinct peaks for melting indicating the formation of two different polymorphs, which were not observed for the rest of the compositions. It is also observed that the Cp values of this composition are generally higher than those of the PEG [16], which may be related to the phase transition of the absorbed PEG within the CNF matrices. An increased C_p elevates the latent heat storage capacity. Similar R values were observed for composites of paraffin with porous carbon materials derived from metal organic gel and boron nitride, n-octadecylamine-functionalized multi-walled carbon nanotubes, and CNT-sponge [45-47].

PCN-L3 (composition made through casting) demonstrated great cyclability with 100 heating-cooling cycles with repeatable of fusion and crystallization enthalpies and temperatures, as indicated in Table S3 and Fig. S7 in the Supplementary Information. Materials such as mineral wool or cellulose that are utilized in building insulation have specific heat capacities ranging from 0.84 to 1.8 J/kg, densities of 0.25–1.8 g/m³ and thermal conductivity values of 0.03–0.04 W/m K. Cellulose insulation has a relatively low thermal conductivity of 0.04 W/m K which is competitive to glass and rock wool insulation [8].

Heat Transfer. Thermal conductivity was observed for PCNs that contained trace amounts of TiO₂ nanoparticles (2% by dry weight), and a PCN without additive. Previously reported thermal conductivity of PEG and TEMPO-CNF composite was 0.040 W/m K [16], similar to PCN without additive. PCN containing TiO2 indicated slightly lower thermal conduction around 0.037 W/m K. A possible explanation for the decrease in thermal conductivity after this addition may be the opacifying effect of the nanoparticles. Zhao et al. [48] studied the effect of TiO₂ in porous composites to absorb radiative heat transfer. The TiO₂ acted as an IR opacifier inside vacuum insulation panels. The composites showed reduced overall thermal conductivity caused by higher ultraviolet refraction by the opacifier and lowered radiative heat absorption. According to the Fourier's Law, conductive heat flux within materials depends on their thermal conductivity and the temperature gradient. However, nonconductive heat transfer processes can also influence the effective heat transfer within porous materials. Convection is negligible within materials of high porosity, such as cryogels and foams. In ambient conditions, radiative heat transfer is considered insignificant for such a highly porous system. However, it should be noted that studies have shown materials with low effective thermal conductivity and densities of porous materials may have higher effects from radiative heat transfer that should be taken into consideration [28]. Additives can change the crystal grain size and orientation within the PCM sample that can affect the thermal conductivity [49].

Thermal camera enabled a visualization of latent heat storage from a light source in the samples and demonstrated resistance to deformation induced by temperature. Initial temperature of the experiment was 24.3 °C, and the dual lamps emitted wavelengths from ultraviolet to infrared, resisting high surface temperatures up to 200 °C. Analyzing heat absorption measured by temperature change against relative time demonstrated qualities of the PCN's passive energy storage ability. Temperatures were measured at the surface and beneath the samples. Inflections in the graph (Fig. 8) indicate apparent phase changes of melting and crystallization. The bottom sensor exhibited relatively low radiation to heat transfer, having a 33.5 °C maximum temperature difference between the surface and bottom sensors; this indicated longer heat transfer and better insulation at just 1.5 cm thickness. Fig. S9 shows the thermal performance of CNF (0.035 W/m K thermal conductivity) under irradiation.

Observable delayed phase changes for both melting and crystallization occurred from the TiO₂ sample (PCN-L3), indicated by inflections in the graph (Fig. 8). PCN-L3 exhibited higher light to heat absorbance. A maximum of 18.3 °C higher heat absorbance was found in the TiO₂ sample when compared to the PCN sample without TiO₂ (PCN-L2). An average higher temperature of absorbance was 9.28 °C; the calculated average and maximum was taken between the range of 71 °C-26 °C. Moreover, the TiO₂ sample was able to hold higher temperatures, longer. PCN-L3 held higher heat storage for 1011 s, or 16.85 min, gained more light to heat transfer at 148 s, and persisted until 1159 s. Overall, both PCN samples displayed successful form stability, indicating no signs of PCM melt leakage (Fig. S10). Secondary interactions such as iondipole, hydrogen bonding, and van der Waals take part in leakage-free physical gelation. The physical network of the gel can restructure via dissociation and reformation of such secondary bonds. Reversibility of these interactions lead to tunable physical properties such resiliency to mechanical damage and improvement of the PCM life cycle [23]. By observing the behavior of the graphs, the broadness of PCN-L3 temperature curve indicated that it held higher passive energy storage, and more optimally, better regulating radiation to heat conversion compared to PCN-L2. Whereas, PCN-L2 indicated better insulation capabilities, as expected.

3.4. Insulation and thermal regulation

A 5x5x5 cm wooden box, simulating indoor temperatures, was installed with three different types of insulation: PCN-L2, PCN-L3 and mineral wool to demonstrate a comparison in heat transfer behavior. The temperature inside the box was measured during a 10-min radiation (heating) period with dual lamps (500 W m^{-2} average light intensity) and during a 20-min consecutive "radiation-off" (cooling) period. Fig. 9 shows a comparison of the thermocouple measurements for thermal and light to heat conversion over relative time from bare wood, PCN- L2, PCN-L3, and mineral wool model house. The maximum temperature for bare wood and mineral wool-insulated wood are almost 10 °C higher than that of the PCNs-insulated models, indicating PCN's improved insulating ability. Moreover, the PCN samples exhibit better temperature regulating ability, having lower heating, and cooling slopes. The TiO₂ containing PCN-L3 displayed a more distinct phase change at \sim 37 °C and took slightly more time to heat compared to PCN-L2. Additionally, PCN-L3 demonstrated its ability to hold heat longer than PCN-L2, suggesting the influence of the additive on the PCN's passive energy storage. One of the biggest advantages of PEG as a PCM is the adjustability of its melting temperature with its molecular weight [16]. The molecular weight of model PEG herein was 4000 g/mol, which melts at 55-60 °C. By reducing the molecular weight to 1000 g/mol and below, the melting can be easily adjusted to around 20-35 °C. This trait facilitates the usage of PEG according to the temperature range needed in the target application. As can be seen in Fig. 9, when the temperature of the insulated object raises within 22–60 $^\circ$ C, which can easily happen under daily irradiation in hot climates, the composite regulates the temperature more effective than that of mineral wool which is a commonly used insulation.

A comparison of insulation materials used in construction is provided



Fig. 8. Thermal camera measurements under irradiation; Core and bottom temperature recorded by thermocouple sensors: comparisons of TiO₂ modified PCN-L3 and unmodified PCN-L2 for radiation to heat conversion and storage over relative time.



Fig. 9. Evaluation of thermal regulation performance of PCN under light irradiation: a) illustration of PCN incorporated in an indoor environment and b) temperature variation measured by thermocouples from experiments presented in Fig. 3.

in Fig. S11 of the Supplementary Information. The combination of PEG and nanocellulose has demonstrated comparable insulating ability and desirable low densities. For instance, other biomaterials that are utilized in building insulation have specific heat capacities ranging from 0.84 to 1.8 J/kg, densities of 0.25–1.8 g/m³ and thermal conductivity values of 0.03–0.04 W/m K. Cellulose insulation has a relatively low thermal conductivity of 0.04 W/m K which is competitive to glass and rock wool insulation. Mineral wool is commonly applied as building insulation with a low thermal conductivity (0.024 W/m K); however, it is quite heavy (70 kg/m³) and poses environmental concerns during extraction and transportation.

4. Conclusions

The PCN cryogels demonstrated appreciable physical and thermal capabilities desirable for a sustainable alternative bio-insulator. PCN composed of different modified CNF and was produced by three different processing techniques that influence form stability, apparent

elasticity, lower weight, decreased thermal conduction and increased passive energy storage. Casting method resulted in the most desired morphological, mechanical, and thermal properties. PCNs were ultralight-weight samples with bulk densities ranging from 0.022 to 0.043 g/cm³, porosities ranging from 95.8 to 98.1%, and volumetric porosity distribution of 2-180 nm pore widths. PCN-L3 showed great height recovery after compressive force, being able to recover 81.7% after 6 N force and 43.8% after 16 N force. The overall average of PCN enthalpy of fusion was 138.4 J/g. Moreover, specific heat capacity was measured to be as high as 2.24 J/g K for PCN-A4. PCN samples modified with trace amounts of TiO2 did not produce significant changes in latent energy storage or Cp but exhibited better thermoregulating abilities indicated by delayed phase changes when applied for insulating an indoor climate. PCN kept its original form and no leakage under high thermal and UV stress. Irradiation tests proved good insulating ability of 33.5 °C temperature protection with just 1.5 cm of PCN material. In ambient conditions, the 0.5 cm of PCN material provided ~ 10 °C increased thermal protection when compared to mineral wool. The PCN

was able to demonstrate thermo-regulation of 2.23 $^{\circ}$ C with 1 mm of PCN material. Finally, the PCN displayed unexpectedly fine acoustic absorbance, and provided 100% absorbance at 1600 Hz, and even 50% at lower frequencies (500 Hz). With further research, PCNs may have potential applications for thermal protection in smart building, electronic, packaging and airplane sectors.

Associated content

A Supplementary Information file is provided including tabulated data and figures of PCN samples, porosity distribution, specific heat capacity, DMA as well as conductivity set-up.

CRediT authorship contribution statement

Wendy T. Le: Writing – original draft, Methodology, Formal analysis, Conceptualization. Ari Kankkunen: Writing – review & editing, Methodology, Formal analysis. Orlando J. Rojas: Writing – review & editing, Supervision, Resources, Conceptualization. Maryam R. Yazdani: Writing – review & editing, Supervision, Resources, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solmat.2023.112337.

Abbreviations

- ACNF Acetylated cellulose nanofibrils
- BET Brunauer–Emmett–Teller Theory
- CNF Cellulose nanofibrils
- DMA Dynamic Mechanical Analysis
- DSC Differential Scanning Calorimetry
- FD Freeze-dry
- FT Freeze-template
- LCNF Lignin cellulose nanofibrils
- PCM phase change nanohybrid
- PEG polyethylene glycol
- SEM scanning electron microscope SDG sustainable development goal
- SDG sustainable development goal
- TEMPO 2,2,6,6-tetramethylpiperidine-1-oxyl
- TiO₂ titanium dioxide.

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