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Cellulose foams as scalable templates for phase change materials

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A B S T R A C T

Cellulose foams produced by wet-templating fibers and surfactants offer an unlimited creative space for the design of green functional materials with a wide range of energy-related applications. Aiming to reduce plastic pollution, cellulose foams promise to replace plastic foams after tailoring physical functionalities into their structures. Here, this work demonstrates that cellulose foams made of methylcellulose and cellulose fibers can exhibit a solid–liquid phase change functionality by adding a phase change material (PCM) during the foam-forming process. The resulting foam composites, termed cellulose phase change foams (PCFs), exhibit a tenth of cellulose's density (134.7 kg m\(^{-3}\)) yet a high Young’s modulus (0.42 MPa). They are also dimensionally stable over a wide range of temperatures while absorbing up to 108 kJ kg\(^{-1}\) as latent heat when the PCM confined to the foam experiences a solid-to-liquid transition at \(\sim 60^\circ\text{C}\), and releasing 108 kJ kg\(^{-1}\) as latent heat when changing from liquid to solid at \(\sim 40^\circ\text{C}\). Such phase change transition opens up broad applications for the PCFs as thermal insulators. For example, by further tuning the transition temperature, the PCFs can exploit their phase change and reduce the heat flow rate through their radial direction at specified temperatures. This article showcases the versatility of the foam-forming process of cellulose to accommodate physical functionalities in materials with complex architectures. Furthermore, thanks to the advances in cellulose foam-forming, such foams are recyclable, industrially scalable, and can be exploited as heat storage materials.

1. Introduction

Foam materials are increasingly in demand for packaging, energy storage, thermal insulation, and sound absorption [1–8]. Nonetheless, typical foam products are based on plastics with environmental drawbacks attributed to their non-renewable origin, energy-intensive manufacturing processes, and unfeasible reincorporation in the biosphere. Today, various green materials are being proposed to replace traditional foams. These new foams mimic the cellular architecture of biological materials, such as wood and cork, achieving high load-bearing yet lightweight structures [1–3,9–13]. As cellulose is the most abundant biodegradable natural polymer, this polysaccharide has become a sustainable and locally available resource for innovating such complex structures [14,15]. Cellulose building blocks (e.g., cellulose pulps, cellulose derivatives, and nanocelluloses) are wet-foamed and further dried resulting in 3D anisotropic porous structures with less than a tenth of cellulose density [3,4,10,11,16–19]. What is most relevant about the so-called “cellulose foams” (see Fig. 1) is their potential use as green and lightweight templates for responsive substances occupying strategic positions in the foam cell wall and voids [1]. For example, cellulose foams have been suggested for detecting external stimuli, tailoring electric conductive materials, and storing energy [5,6,20–22]. In particular, as we present, cellulose foams endow confining a phase change material (PCM), creating a foam composite for thermal insulation capable of storing and releasing a high thermal energy density [5,23,24].

Cellulose is the main reinforcing component of the cell wall in plants. As a raw material, cellulose has recently collected growing interest in developing energy-related technologies [25–29]. Its popularity stems from its biodegradable and renewable nature and properties—cellulose is mechanically strong, as well as chemically and thermally stable [14,30]. In energy storage materials, cellulose substrates are widely used as templates for electric carriers and electroactive materials [26]. While in terms of thermal energy storage applications, cellulose has been lately exploited to develop functional hollow fibers, hydrogels, and films, where cellulose provides a supporting matrix for PCMs, such as organic paraffin, polyethylene oxide (PEO), and polyethylene glycol (PEG) [31–33]. In particular, when heating the latter functional composites, they feature solid–liquid (i.e., crystalline to amorphous and vice versa) transition temperatures during which

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the PCM stores energy as latent heat and releases it at near room temperatures. In the phase change systems, cellulose templates grant efficient PCM confinement and avoid leakage when the latter dynamically changes between the crystalline and amorphous states \[23,31–36\]. Such novel latent heat storage materials have high energy storage density, which is thought to help reduce imbalances between energy consumption and energy supply by creating “smart” thermal insulation systems \[6\].

Recent advances in thermal insulation technologies suggest adjusting the phase transition temperature of PCMs to near room temperature for reducing parasitic heat loss and gain in buildings, wearables, and electric vehicles \[23,24,32,37,38\]. Intrinsically, the nature of such applications demands lightweight, sustainable, and affordable solutions competitive with traditional plastic insulation foams (e.g., polyurethane and polystyrene foams) \[24\]. PEG being a compatible material with cellulose building blocks, this polyether is attractive for tailoring functional green composites for thermal energy conservation \[23,31,39\]. During its solid–liquid (crystalline-amorphous) transition, PEG stores up to \(\sim 230 \text{ kJ kg}^{-1}\) as latent heat, the exact value depending on the molar mass of the biopolymer \[23,31,39,40\]. Besides its latent heat capacity, PEG has high cyclability and a tunable transition temperature, which can be adjusted to the desired working conditions \[31,40,41\]. Therefore, (physically) functionalizing the cellular structure of cellulose foams could be advantageous for creating smart thermal regulation systems with low thermal conduction.

As an example of the synergy between cellulose and a PCM, Lee et al. \[32\] developed a cellulose-PCM material with phase transition at 25 \(^\circ\)C and tested it in the walls of a building; the results showed energy savings and thermal comfort improvements. Developing a cellulose phase change foam (PCF) benefits from the energy-efficient production and property-weight ratio of foam-formed cellulose materials \[10\]. For instance, cellulose foams with relative densities of \(\sim 0.02\) have demonstrated low thermal conductivity, as well as compressive strength comparable to ceramic foams \[3,20\]. Since cellulose and other foam structures have previously confined and stabilized PCMs, cellulose foams have outstanding potential as green templates for PCMs with a solid–liquid transition \[31,32,39,42,43\]. Compared to other methods used to confine a PCM and avoid its leakage at high temperatures (e.g., carbon foams and nanocellulose), PCFs would represent a scalable technology with high production volumes. In previous works, we reported on a scalable manufacturing process for fabricating cellulose foams recyclable with cardboard and paper; the process is now in the start-up stage and can incorporate recycled raw materials \[3,44\].

Here, we report a simple approach to manufacturing PCFs via additive manufacturing using a wet foam templating technique \[3,44\]. We hypothesize, first, that we can create a phase change cellulose foam by including PEG in the wet foaming process of methylcellulose (MC) and cellulose fibers (CF) obtained from leftovers of wheat straw crops. In this approach, the MC, CF, and PEG develop...
a stable phase due to the dipole–dipole interactions between hydroxyl groups, preventing PCM leakage during its dynamic solid–liquid transition. To the best of our knowledge, cellulose foams as green templates to retain PEG have not been previously reported. Our objective is to manufacture a green thermal energy storage material using sustainable raw materials in line with the new bioeconomy models adopted by the European Union [45,46]. To illustrate the simple processing and materials properties of the PCFs, we produced and characterized five foams with PEG content (c) ranging from 33 to 66 wt.%. The PCFs show unique mechanical and thermal properties, helping us expand the research path to upscale production and use them as lightweight thermal insulation between closed surfaces.

2. Materials and methods

Preparing the PCFs requires high molecular weight methylecellulose (MC) which we acquired from Ashland Specialties Belgium. This MC has a bimodal molar mass distribution with a weight average molecular weight (Mw) of 534 kg mol⁻¹ (polydispersity index 1.5) and a degree of substitution for CH2 of approximately 1.87 [47]. Bleached wheat straw pulp (Fortum, Finland) reinforced the foam structure and enhanced the tortuosity of the medium. The pulp comprises of short cellulose fibers with an arithmetic mean length of 0.3 mm and width of 17.21 μm (fiber properties measured with a Valmet Fiber Analyzer). In addition, PEG with a number average molecular weight (Mn) of 8 kg mol⁻¹ (PEG 8000, Sigma Aldrich) was used to tailor the phase change functionalities in the cellulose foams. For all purposes, sample preparation utilized high-purity Milli-Q water with a resistivity of 18 MΩ cm. This article reports and discusses the results for five PCFs, and Table 1 summarizes their composition. The sample labeling describes the PEG content in the dried foam. For example, PCF-54 stands for a cellulose foam containing 54 wt.% PEG.

2.1. Fabrication of the phase change cellulose foams

MC and PEG were dispersed in water at 50 °C for each sample and stirred for 20 min. The aqueous mixture was cooled to 30 °C by natural convection; then, cellulose fibers were incorporated into the mixture as Table 1 indicates. The suspensions were tempered overnight at 3 °C. The foaming of the suspensions continued through the Hele-Shaw flow between two syringes connected; one syringe contained 30 ml of suspension, and the other contained a free volume of 30 ml. Producing the wet foam stems from exchanging the suspension a few times from one syringe to the other until the volume of the wet foam reaches 60 ml. We fabricated PCF sheets by printing hydrogel-like wet foam structures shaped in rods, which are dried with a heating lamp and then glued on each other by spraying deionized water on the sheet surface [3].

2.2. Small amplitude oscillatory shear

In an MCR 302 rheometer (Anton Paar, Austria), small amplitude oscillatory shear (SAOS) tests assisted in measuring the rheological properties of the foam precursor suspensions. Rheological experiments (triplicated) required a serrated concentric cylinder geometry, as Fig. 1a illustrates. The bob (CC17/P6) applied to the suspension an oscillatory strain (γ) of 0.5% with an angular frequency (ω) of 10 rad s⁻¹. Controlling the temperature (T) during each experiment employed a Peltier device (C-PTD 180/AIR), which heated the specimens at a 1 °C min⁻¹ rate from 15 to 90 °C. According to the theory of linear viscoelasticity, SAOS experiments record a complex signal with an in-phase and out-of-phase component, corresponding to the storage shear modulus (G') and loss shear modulus (G''). The complex signal itself is the dynamic shear modulus (Gd), which is the magnitude of the complex shear modulus (G'). Eq. (1) defines Gd as terms of G' and G'' as

\[ G_d(\omega, T) = \sqrt{G'(\omega, T)^2 + G''(\omega, T)^2} \]  

(1)

The lower critical solution temperature (LCST) transition of MC allows printing the wet cellulose foam without collapsing its cell structure, see Fig. 1b and Fig. 1c. Therefore, from the SAOS experimental data, the transition temperature (Tc) of the suspensions is calculated according to a method previously reported [47]. In short, Tc is extracted from the phase shift angle (δ) as a function of T. δ defines the viscoelastic behavior of a material, so an abrupt change in δ as a function of T is expressed when a material transitions from a viscoelastic liquid (δ > 0) to a viscoelastic solid (δ < π/2). In terms of G' and G'', Eq. (2) defines δ as

\[ \delta(\omega, T) = \arctan \left( \frac{G''(\omega, T)}{G'(\omega, T)} \right) \]  

(2)

where the inverse function tan δ is the loss factor related to energy dissipation through molecular frictions in a viscoelastic material [48]. The experimental data were processed using the Machine Learning framework previously reported [47], which uses a Bayesian optimization approach with a Gaussian predictor.

2.3. Scanning electron microscopy

With SEM, the architecture of the foam cells of two samples (PCF-33 and PCF-60) was imaged using a Sigma VP (Zeiss, Germany) scanning electron microscope (SEM). For the analysis, a thin layer of Au/Pd 80/20 was sprayed on the foam surface using a Q 150R S plus sputter coater (Quorum, United Kingdom). Additionally, to enhance the conductivity of the samples, they were mounted on conductive carbon tape. The electric potential stayed at 3.0 keV, and images were obtained from the backscattered secondary electron signal (SE2).

2.4. Fourier transform infrared spectra

High-resolution infrared spectra were obtained using attenuated total reflectance (ATR) for all PCFs and a reference foam without PEG. The device used was a Spectrum TwoTM LiTaO₃ (Perkin Elmer, United Kingdom) and an ATR instrument (Specac Quest, United Kingdom). All measurements were performed at room temperature by scanning 90 times the wavenumber (υ) interval from 4000 to 500 cm⁻¹. The spectra were normalized to their absorption (A) at 1056 cm⁻¹.

2.5. Uniaxial compression

The static mechanical properties of the PCFs were measured in an Electrolux® E1000 testing machine (Instron, United Kingdom). We compressed foam specimens of 15 mm per side at a deformation rate of 30 mm min⁻¹ in the radial direction of the cellular structure (five specimens per sample), see Fig. 1d. Stress–strain (σ – ε) curves illustrate the compressive behavior of the PCFs. The Young’s modulus (E) computation proceeded by fitting a linear function in the range of 20 % strain within the elastic region, as exemplified in Figure S1. The experimental data were processed using the Machine Learning framework previously reported [47].

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>MC [wt.%)</th>
<th>CF [wt.%)</th>
<th>PEG [wt.%)</th>
<th>Water [wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCF-33</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
<td>95.50</td>
</tr>
<tr>
<td>PCF-43</td>
<td>1.50</td>
<td>1.50</td>
<td>2.25</td>
<td>94.75</td>
</tr>
<tr>
<td>PCF-54</td>
<td>1.50</td>
<td>1.50</td>
<td>3.50</td>
<td>93.50</td>
</tr>
<tr>
<td>PCF-60</td>
<td>1.50</td>
<td>1.50</td>
<td>4.50</td>
<td>92.50</td>
</tr>
<tr>
<td>PCF-66</td>
<td>1.50</td>
<td>1.50</td>
<td>6.00</td>
<td>91.00</td>
</tr>
</tbody>
</table>

The device used was a Spectrum TwoTM LiTaO₃ (Perkin Elmer, United Kingdom) and an ATR instrument (Specac Quest, United Kingdom). All measurements were performed at room temperature by scanning 90 times the wavenumber (υ) interval from 4000 to 500 cm⁻¹. The spectra were normalized to their absorption (A) at 1056 cm⁻¹.
2.6. Dynamic mechanical thermal analysis

The dynamic analysis of the PCFs was done in a Rheometer Dynamic Mechanical Analyzer MCR 702e (Anton Paar, Austria). Similarly to the approach described for SAOS experiments, dynamic mechanical thermal analysis (DMTA) follows the theory of linear viscoelasticity. Thus, foam samples (15 mm per side and three specimens per sample) were dynamically compressed (PP25 and L-PP25/TD/TS geometry) in their radial direction, applying a peak of 1% with ω of 10 rad s⁻¹. From the DMTA experiments, a complex signal is obtained as a function of T by heating the sample at 1 °C min⁻¹ from 30 to 90 °C. Homogeneous foam heating is ensured by using a CTD-180 convection oven, which adjusts the temperature gradient between the oven walls and the L-PP25 plate, measuring the temperature of the foam.

The complex signal generated from the test has an in-phase and an out-of-phase component, corresponding to the storage modulus (E′) and the loss modulus (E″). The complex signal is defined as the dynamic modulus (Eₒ), the magnitude of the complex modulus (E)*. Eq. (3) defines Eₒ in terms of E′ and E″ as

\[ Eₒ(ω, T) = \sqrt{[E′(ω, T)]^2 + [E″(ω, T)]^2}. \tag{3} \]

Analogously to Eq. (2), for DMTA tests, δ is expressed in terms of E′ and E″ as

\[ \delta(ω, T) = \arctan \frac{E″(ω, T)}{E'(ω, T)}. \tag{4} \]

From the DMTA tests, the phase change temperature (T_p) of the PCFs can be estimated from E′. Assuming that E′ represents the elastic forces in a PCF, a steep decay in E′ indicates the transition from a crystalline to an amorphous state, occurring when the PEG melts and becomes a viscoelastic fluid confined to the foam structure. Hence, T_p is where the E′ decay is equidistant from the upper and lower tangents.

2.7. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to measure the heat energy storage capacity of the PCFs. Therefore, a DSC250 thermal analyzer (TA Instruments, USA) performed the calorimetry experiments (triplicated per sample) by heating and cooling the PCF samples from −10 to 90 °C (three cycles and sample mass ~9 mg) at 5 °C min⁻¹. All experiments proceeded under a protective nitrogen gas atmosphere (50 ml min⁻¹) and using a reference aluminum pan. We defined the melting temperature (T_m) and crystallization temperature (T_c) of the PCFs from the peak maximum during the heating and cooling cycles, respectively. The specific latent heat of melting (L_m) and the specific latent heat of crystallization (L_c) are the results of integrating over their corresponding peaks. The first heating-cooling cycle is discarded as its objective is to erase the thermal history and stresses in the material. In this manuscript, we report the results of the second heating-cooling cycle.

2.8. Thermal imaging

To measure the temperature profile in the radial direction, PCF specimens were mounted on an aluminum plate with a diameter of 50 mm and Peltier temperature control. The temperature was controlled using an MCR 302 rheometer (Anton Paar, Austria), and the experiment was recorded using a FLIR A315 infrared camera (FLIR, Sweden); a similar methodology has been reported elsewhere [3,49]. Before starting the experiment, the heating stage was stabilized at 60 °C for 2 h, leading to an accuracy of ± 0.01 °C. It is assumed that aluminum’s heat conductivity is higher than the PCFs heat conductivity. The infrared camera followed the heat transport in the radial direction of the PCF specimens (15 mm per side) by taking images (320 pixels × 240 pixels) at a frame rate of 5 Hz. The camera has accuracy and thermal sensitivity ± 2 °C and 0.05 °C, respectively. The weight loss during heating was minimal, according to DMTA observations. The thermal profile along the radial direction of the foam was measured using the camera software Thermacam™, provided by the manufacturer.

3. Results and discussion

PCFs were successfully produced through the aqueous dispersion and foaming of MC, cellulose fibers, and PEG. Fig. 1a shows the appearance of the precursor suspension before foaming. Fig. 1b illustrates the printing and simultaneous drying of the wet foam. Then, Fig. 1c depicts an example of PCF, from which foam blocks, such as the one in Fig. 1d, were cut and characterized. Therefore, we have proved our first hypothesis that PEG does not hinder the foamability of cellulose products. However, the maximum concentration of PEG in the PCFs was restricted to 66 wt.% since higher concentrations hindered the foaming behavior of the methylcellulose surfactant, limiting the maximum energy storage of the material (which depends on the PEG content). In contrast, the lowest concentration of PEG was 33 wt.%, as lower concentrations than that do not achieve the desired thermal performance in terms of latent heat. The maximum PCM content reached here is higher than that reported in some cement mixtures, where the PCM content has been limited to 20 wt.%, and in the range achieved using other inorganic supporting materials such as diatomite [50–52]. Compared to other cellulose-based PCM composites, our maximum PCM content was between the range reported in the literature, from 40 to 90 wt.% [23,32,34]. With further optimization of the methylcellulose and cellulose fiber contents, it would be possible to exploit higher PEG concentrations, and therefore, higher latent heats. Macroscopically, we produced PCF blocks (270 mm × 100 mm × 15 mm) with dimensional stability. The scanning electron microscopy (SEM) images in Fig. 1e and Figure S3 show that the PCFs had a cellular structure composed of closed cells, which are elongated in the longitudinal direction of the foam structure. To the best of our knowledge, this is the first report on a phase change cellulose foam manufactured by incorporating PEG into the foam-forming process of cellulose-based materials. In the following sections, we characterize the mechanical, thermomechanical, and thermal properties of the PCFs to prove our second and third hypotheses and demonstrate that the PCFs exhibit mechanical, thermomechanical, and thermal properties relevant to creating sustainable thermal insulation materials.

3.1. Foam structure and compressive behavior

In fabricating cellulose foams based on aqueous dispersions of MC and cellulose fibers, foaming and printing are highly dependent on the rheological gel transition temperature (T_g) of MC [47]. The transition is believed to occur when polymer chains percolate and form a physically crosslinked hydrogel fibril network (thermogelation) [47,53]. MC thermogelation turns the precursor wet foam system into a viscoelastic solid, allowing 3D printing and dry dimensionally stable foam rods, such as the one depicted in Fig. 1b. Therefore, the rheological characterization via small amplitude oscillatory (SAOS) tests of the aqueous dispersion to be foamed allows us to assess the effect of PEG on the viscoelastic properties of the precursor foam system. In general, as Fig. 2a illustrates, increasing c in the precursor suspension reduces the elastic (G′) and viscous (G′′) components of the dynamic shear modulus (G*) of the latter occurs because loading the system with PEG reduces the free space for MC polymer chains, which, due to their high weight average molecular weight (M_w), tends to control the viscoelastic properties of the suspension. Thus, when c is higher, the polyether exhibits viscoelastic properties, which are of a lower magnitude than those of MC.

To estimate the effect of PEG on the transition temperature, Fig. 2b shows a surface created by applying Bayesian optimization with a Gaussian predictor to the experimental data of the phase shift angle (δ). The results predicted in Fig. 2c allow us to infer the relationship between c and T_g of the system with a reduced number of PEG concentrations. Machine Learning shows its potential to characterize non-linear behaviors, which in materials research represents savings in time and resources. In other words, Machine Learning helps to
explore the parameter \( c \) efficiently, compared to traditional Design of Experiments (DoE) approaches, which require several experiments to explore the experimental space [54]. \( T_r \) decreases as a function of \( c \), implying that the polyether decreases the activation energy of the thermogelation process. What is most important, as long as \( G' \) does not drop lower than 50 Pa, PEG can be combined with MC and cellulose fibers to fabricate a dry foam. The OH groups of the PEG chains can associate with the OH groups of MC and cellulose fibers [31,55]. Consequently, the probability of forming physical crosslinks at lower temperatures increases, as has been described for other gel-forming systems [47,55,56]. In terms of energy efficiency, a lower \( T_r \) represents a reduction in the energy required to dry the foam. Therefore, adding PEG to any cellulose-based foaming process is a promising solution to reducing energy consumption when upscaling cellulose foam production [47,59]. In material properties than \( T_r \), as we suggested in a previous article [47].

To observe the relationship between \( c \) and \( E \), the experimental compression results were processed with the same Machine Learning algorithm used to estimate \( T_r \) in Fig. 2c. The surface created in Fig. 2e results from interpolating the experimental \( \sigma - \varepsilon \) curves of the PCFs. This occurs due to the increase in foam density (\( \rho \)) as a function of \( c \). When the foam is compressed, the material has less free volume, leading to premature cell collapse. At the same time, as Table 2 shows, the \( E/\rho \) index of the PCFs follows the same trend; it increases with the PEG concentration. Calculating the \( E/\rho \) index for the PCFs shows that the reinforcement of mechanical properties comes from favorable interactions between all the PCF constituents and not only due to an increment in the solid content. A similar effect has been reported when lignin is added to cellulose foams; cellulose and lignin interact via intermolecular forces [44]. Given the polar nature of PEG, MC, and cellulose fibers in the PCFs, they can interact via hydrogen bonding, thus reinforcing the foam structure.

After rheological characterization of the wet suspensions, the PCFs were produced and characterized. All PCFs had an elongated closed cell foam structure similar to the cellular structure of wood, as Fig. 1e exemplifies. Foam cells are oriented toward the printing direction, which is typical of open mold foaming processes; see Fig. 1b [3,57]. The static mechanical properties of the PCFs were tested in uniaxial compression over the radial direction (perpendicular to the foam cell elongation). Fig. 2d illustrates the experimental results as stress–strain (\( \sigma - \varepsilon \)) curves. The PCFs had compression profiles typical of elastomeric foams. In other words, the foams exhibited elastic behavior under small deformations, followed by a stress onset due to the collapse of the foam structure [57,58]. From Fig. 2d it is possible to see that the stress onset changed to lower values of \( \varepsilon \) as \( c \) increased in the foam.
can be related to the increasing foam density (Table 2) and cell wall thickening. Figure S3 illustrates the difference between the cell structure of PCF-33 and PCF-60, showing that the cell wall thickens after increasing c in the foam. It is worth mentioning that the PCFs are anisotropic, and E of the longitudinal direction is typically ten times greater than the measured in the radial direction; see Figure S2 [3]. Our PCFs displayed a great load-bearing capacity comparable to other polymer foams, yet lower than that of PCM composites with inorganic matrices [2,3,51,52]. For example, the compressive strength of a PCM board made using gypsum was reported as 3.9 MPa, while here PCF-66 displayed a compressive strength of 0.05 MPa. Hence, in terms of mechanical properties, we support our third hypothesis by showing that the PCFs are stiff materials with Young’s moduli in the range of other polymer foams based on cellulose and plastics [19,44,57].

### 3.2. Thermomechanical dynamic properties

The thermomechanical properties of the PCFs were measured using dynamic mechanical thermal analysis (DMTA). Such results describe the performance of the bulk foam, from where we can assess the form stability and possible leakage of PEG when this turns into a liquid. Fig. 3a and Fig. 3b depict the viscoelastic responses of the PCFs as a function of the temperature (T). Both plots demonstrate profiles similar to those observed in polymers when they experience a glass transition [60,61]. The decay in the dynamic modulus (E’), storage modulus (E’’), and loss modulus (E”’) as a function of T is related to the melting of the PEG crystallites; crystal domains are exemplified in Fig. 1f. Furthermore, the point where viscoelastic properties decrease shifts to higher temperatures when c in the PCFs is higher. The shift to higher temperatures is correlated to the mass and heat transfer phenomena restricting the motion of the molecular segments.

Interestingly, the results of the loss factor (tan δ) in Fig. 3e resemble the behavior observed in viscoelastic materials with confined compliant (damping) phases [62,63]. For example, energy dissipation has been shown to increase when an elastomer confines a liquid polymer phase [62]. In the case of the PCFs, the energy dissipation (tan δ) increment as a function of c stems from strong internal frictions occurring when PEG transitions from a crystalline to an amorphous state. However, the damping effect in the PCFs is not particularly high, as tan δ is lower than 0.30 in all cases. Since the PCFs display tan δ < 1, it is possible to tell that the foams retain their elastic properties, which gives them dimensional stability at temperatures higher than the phase transition temperature (Tg). The dimensional stability is also supported by the plateau in E’, E’’), and tan δ after ~60 °C. The latter indicates that no further changes occur in the PCFs after Tg and the PCFs retain their dimensions even after experiencing the phase transition, as we proposed in our third hypothesis about the dimensional stability.

The PCFs can be described as elastomeric cellulose foams that confine a dynamic PEG phase to a cellular structure. PEG is restricted to the cellulose foam template through van der Waals interactions between the OH groups of PEG and cellulose-based macromolecules as well as through secondary interactions between the hydrophobic sites of MC and PEG. The Fourier transform infrared spectra (FTIR) in Figure S4 confirm these dipole–dipole interactions between OH groups since the band at 3600–3100 cm⁻¹ (–O–H stretching vibration) reduces in intensity when PEG is present in the PCF. The interactions between OH groups affect the FTIR by broadening the –O–H band and shifting it to lower frequencies [31]. A similar confinement mechanism has been reported for an organogel composed of cellulose nanofibrils and PEG, where the two polymers interact via hydrogen bonding [31]. The secondary hydrophobic interactions are evident in the FTIR substitution region of MC (3100–2700 cm⁻¹), where the spectrum for PCF-66 (Figure S4) exhibits a change in shape and intensity. Furthermore, cellulose foams restrict the flow of melted PEG as they possess a complex geometry that enhances the tortuosity of the medium. Figure S5 shows a cell in PCF-66, where cellulose fibers occupy the plateau border of the cell and prevent PEG leakage. It has been suggested that due to the amphiphilic nature of cellulose, they can adsorb polar liquids, such as melted PEG [64]. The relevance of such PCFs is that i) their transition temperature can be tuned, ii) they are produced sustainably using recycled and renewable resources, iii) they can be used to fill large volumes, such as walls and other surfaces, reducing the heat transfer rate through different systems, iv) they are recyclable with paper and cardboard, and v) by using recycled fibers, they exhibit similar mechanical performance as cellulose foams based on nanocellulose [3,19].

### 3.3. Thermal properties

As stated in our third hypothesis, including PEG in the cellulose foam allowed us to successfully fabricate heat storage/release systems. The latent heat of the PCFs is summarized in Table 2 after testing the foams with differential scanning calorimetry (DSC). The thermal properties depended on c (i.e., the PEG content). Fig. 3d depicts the second heating cycle of the PCFs, where the normalized heat flow (Q) peaks sharpen and increase as a function of c. In this article, we report only the results for the second heating-cooling cycle; the third cycle showed no significant changes in the energy storage and release capacity of the PCFs. Table 2 and Fig. 3e show that increasing c in the PCFs yields higher energy storage and release (as latent heat) capacity during melting (Lm) and crystallization (Lc), respectively. Here, we restricted c to the 33-66 wt% range. PEG concentrations lower than 33 wt.% had Lm less than 22 kJ kg⁻¹, energy storage capacities that are too low for the scope of this article. In the future, it is possible to reach higher c than 66 wt.% in the PCFs; however, we will need to find the optimal MC concentration allowing the foaming process.

In general, low PEG concentrations in the PCFs led to latent heats of a lower magnitude than the theoretical ones. For example, PCF-33 had a Lm of 22.64 kJ kg⁻¹. According to the measured Lm of PEG (174 kJ kg⁻¹) in Fig. 3e, PCF-33 should have had a Lm close to 57 kJ kg⁻¹. The difference between the theoretical and experimental value of Lm could be attributed to the presence of nonreactive PCM due to strong intramolecular interactions with the matrix foam when c is low. This issue is solved as c takes larger values in the PCFs, as we observed for PCF-66, whose experimental and theoretical Lm differ only by 6 kJ kg⁻¹. The latter confirms that the cellulose foam
Fig. 3. Thermal properties of the phase change cellulose foams (PCFs). Dynamic mechanical thermal analysis (DMTA) results are expressed in terms of (a) dynamic modulus ($E_d$), (b) storage modulus ($E'$) and loss modulus ($E''$), and (c) loss factor ($\tan \delta$). Differential scanning calorimetry (DSC) results of the PCFs showing a (d) 3D plot of the normalized heat flow ($Q$) (heating) thermogram as a function of polyethylene glycol (PEG) content ($c$), and (e) specific latent heat ($L$) of the PCFs (the open symbol (◦) is the latent heat of pure PEG). Thermal imaging of the PCFs illustrating the (f) heat transfer in the radial direction (open and filled: reference and PCF-66, respectively), and (g) experimental setup [3,49].

Template does not hinder the enthalpy of change of PEG. Furthermore, to confirm that PEG does not leak out the PCFs, we measured the latent heat capacity of a PCF-66 specimen tested previously with DMTA; $L_m$ and $L_c$ showed no significant difference with the values reported in Table 2 ($\sim$107 kJ kg$^{-1}$). Therefore, the stored heat in PCFs ranged from 22 kJ kg$^{-1}$ to 108 kJ kg$^{-1}$, whereas the heat released was from $-20$ to $-109$ kJ kg$^{-1}$. The differences between the measured $L_m$ and $L_c$ are too small to distinguish from the standard deviation. Still, the difference is typically associated with the specific heat capacities of PEG in the solid and liquid states [31].

The melting temperatures ($T_m$) of the PCFs measured with DSC were in the same range as $T_p$, confirming that extracting the transition temperature from $E''$ gives an accurate estimation. $T_m$ ranges from 57 to 62 °C, increasing as a function of $c$. Analogously to the explanation given for $T_p$, the melting temperature shifts to higher temperatures because of mass and heat transfer phenomena restricting the motion of the molecular segments. On the contrary, the crystallization temperatures ($T_c$) in Table 2 change drastically as $c$ increases in the PCFs. $T_c$ increased from 28 to 40 °C as a function of $c$. $T_c$ is different than $T_m$ because of the crystallization kinetics of PEG [65]. In general, the thermal properties achieved by the PCFs compete with current PCM solutions using paraffin and PEG [31,32,66]. Table 3 compares the thermal properties of the PCFs against other solutions confining PCMs with a solid–liquid transition. From Table 3, one can see that cellulose and PEG have a great synergy for developing PCM composites. The literature reports various PCM composites using cellulose and PEG, for example, gels, films, and fibers; these materials show high latent heat of melting, surpassing 100 kJ kg$^{-1}$ [31,35,36]. Here we have expanded further the synergy between cellulose and PEG to produce foams. The advantage of the PCFs reported here against other solutions...
using cellulose as template is that they can be produced in industrial-level volumes; this is compared with proposed technologies using gels and films to confine PEG [31,35,67]. The reported PCFs are sustainable, dimensionally stable, and tunable; the transition temperature can be decreased using PEGs of lower number average molecular weight (M<sub>n</sub>).

In contrast with PCM composites using gypsum or cement as a support matrix, cellulose allows achieving lighter materials [50,51]. For example, PCM gypsum boards can exhibit 530 kg m<sup>−2</sup> as apparent density while here the maximum density of the PCF was 134.7 kg m<sup>−3</sup> [51]. Nevertheless, one should highlight that PCM composites using inorganic matrices exhibit higher mechanical performance and can also be produced on large industrial scales. Therefore, choosing between PCM composites with organic and inorganic matrices should consider the target application and its sustainability.

Finally, we assessed the thermal conduction properties of the PCFs. Fig. 3f shows the temperature profile in one dimension (radial) of a PCF-66 specimen against a reference foam without PEG. Fig. 3g is an example of a thermal image used to estimate the temperature profile. The temperature profile is expressed in terms of T<sup>*</sup>, which is defined in Eq. (5) as

\[
T^* = \frac{T(y) - T_i}{T_2 - T_1},
\]

where T(y) is the temperature as a function of the distance from the surface in contact with the heating plate to the top surface of the foam. T<sub>i</sub> is the room temperature and T<sub>2</sub> is the temperature of the heating plate. With the results in Fig. 3f, we demonstrate pragmatically the relevance of adding PEG in the PCFs, as the phase transition delays the heat flow through the foam since T<sup>*</sup> has a steeper decrease when the foam contains PEG. The same delay effect could be used to improve thermal insulation in building walls by adjusting the transition near the outdoor temperature; however, further experiments are required to optimize for this. Here, we achieved our objective by successfully manufacturing a phase change cellulose foam with relevance as a green and lightweight thermal insulation material.

4. Conclusions

This work showed that PEG could be included in the foam-forming process of cellulose products, reducing the gelation temperature and, therefore, the energy intensiveness of the manufacturing process. As a PCM with a solid–liquid transition, PEG has restricted use in energy storage technologies since the polymer melts and leaks out at temperatures above its phase transition. However, the PCFs designed here have been shown to prevent PEG leakage and retain their dimensionally stability at temperatures above T<sub>f</sub>. The PCFs can be described as elastomeric foams that can confine a liquid polymer phase through supramolecular interactions between the hydrophobic sites and OH groups of cellulose-based materials and PEG. Furthermore, the confinement mechanism is supported by the complex and tortuous medium inside the PCFs, which is enhanced by cellulose fibers organizing in the plateau borders of the foam cells. In terms of thermal performance, we achieved a PCF with L<sub>m</sub> of 108 kJ kg<sup>−1</sup> and a melting temperature of ∼60 °C.

The outstanding thermal performance of the PCFs is accompanied by mechanical properties that make the material stiff. In the radial direction, PCF-66 displayed an E of 0.42 MPa, and in the longitudinal direction, an E of 7.02 MPa, values in the typical range for polymer foams. The Machine Learning algorithm demonstrated its potential to speed up materials research, allowing one to characterize non-linear behaviors with few experiments. In the future, the same Machine Learning algorithm can be used as an “adaptive sampling” or “active learning” technique to optimize the PEG content and molar mass to produce PCFs for specific applications. In summary, we proved our three hypotheses: (i) PEG can be used to create PCFs; (ii) Machine Learning allows the characterization of non-linear behavior with a few experiments; (iii) cellulose foams granted effective confinement of PEG, creating a dimensionally stable PCF that stores and releases latent heat. Furthermore, due to the scalability of the foam manufacturing process used here and the possibility of modifying the phase transition temperature, the PCFs show the potential to become sustainable insulation materials for reducing the heat flow rate between surfaces in residential buildings, wearables, and vehicles.

Table 3

Comparison between cellulose-based phase change material composites in the literature and the performance of the phase change foam reported in this article. PEG and polyethylene oxide (PEO) are polymers with the same chemical structure; their difference is their molecular weight.

<table>
<thead>
<tr>
<th>Phase change material</th>
<th>Polymer matrix</th>
<th>Description</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; [°C]</th>
<th>L&lt;sub&gt;m&lt;/sub&gt; [kJ kg&lt;sup&gt;−1&lt;/sup&gt;]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>paraffin (42 wt.%)</td>
<td>cellulose</td>
<td>insulation material</td>
<td>25</td>
<td>61</td>
<td>[22]</td>
</tr>
<tr>
<td>PEG800 (80 wt.%)</td>
<td>wood based</td>
<td>porous material</td>
<td>31</td>
<td>134</td>
<td>[21]</td>
</tr>
<tr>
<td>PEG8000 (85 wt.%)</td>
<td>nanocellulose</td>
<td>organogel</td>
<td>65</td>
<td>146</td>
<td>[31]</td>
</tr>
<tr>
<td>PEG4000 (60 wt.%)</td>
<td>cellulose</td>
<td>casted film</td>
<td>58</td>
<td>85</td>
<td>[35]</td>
</tr>
<tr>
<td>PEO (75 wt.%)</td>
<td>cellulose</td>
<td>casted film</td>
<td>63</td>
<td>135</td>
<td>[32]</td>
</tr>
<tr>
<td>PEO (75 wt.%)</td>
<td>cellulose ether</td>
<td>casted film</td>
<td>58</td>
<td>140</td>
<td>[33]</td>
</tr>
<tr>
<td>PEG5000 (90 wt.%)</td>
<td>cellulose</td>
<td>casted film</td>
<td>59</td>
<td>171</td>
<td>[34]</td>
</tr>
<tr>
<td>PEG10000 (70 wt.%)</td>
<td>cellulose ether</td>
<td>casted film</td>
<td>61</td>
<td>120</td>
<td>[36]</td>
</tr>
<tr>
<td>PEG8000 (66 wt.%)</td>
<td>cellulose ether</td>
<td>elastomeric foam</td>
<td>60</td>
<td>108</td>
<td>this work</td>
</tr>
</tbody>
</table>

CRediT authorship contribution statement

Isaac Y. Miranda-Valdez: Conceptualization, Methodology, Software, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. Maryam Roza Yazdani: Conceptualization, Resources, Validation, Supervision, Writing – review & editing. Tero Mäkinen: Validation, Supervision, Writing – review & editing. Sebastian Coffeng: Investigation. Leevi Viitanen: Software. Juha Koivistio: Conceptualization, Supervision, Validation, Writing – review & editing, Funding acquisition. Mikko J. Alava: Conceptualization, Supervision, Validation, Writing – review & editing, Funding acquisition, Project administration.

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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