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Research Papers

Water-resistant gum-based phase change composite for thermo-regulating insulation packaging

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ABSTRACT

The world’s current energy crisis calls for green energy solutions that can preserve energy while incorporating renewable. As such, we have developed a leakage-proof phase change material (PCM) embedded in a biopolymeric matrix as a lightweight yet strong bio-based phase change composite (PCC) for passive energy storage and insulation purposes in packaging. This bio-based composite consists of gum tragacanth (GT) biopolymer and polyethylene glycol (PEG) PCM. It is further incorporated with biochar (BC) or mineral additive, i.e., Cloisite Na+, to enhance its mechanical strength and thermal stability, which are among the main challenges for insulation materials. A hydrophobic layer of octadecyl isocyanate (ODI) is developed on the surface of the composite to increase its water resistance. The composite provides a hydrophobic surface with a minor water uptake capacity of 3.6 ± 0.3 % after one-week immersion in the water. It shows high latent heat storage up to 160 J g−1 and a stable phase change behavior, as demonstrated by over 100 differential scanning calorimetry heating-cooling cycles. It also possesses notable compressive mechanical properties, which were improved significantly after incorporating BC and Cloisite Na+. The thermal conductivity of the composite is as low as 0.035 W m−1 K−1 manifesting in better thermal regulation compared with commercial polyethylene foams. This energy-positive bio-based solution combines the advantages of excellent insulation as a highly porous, lightweight, and strong composite with the latent heat and thermal inertia of PCM, making it suitable for transportation packaging of temperature-sensitive products.

1. Introduction

Heat flows as a result of a temperature difference between materials, while thermal insulation can inhibit the heat transfer between the materials where needed. Insulation materials are widely used in various areas of daily life, including electronics, buildings, packaging, transportation, etc. For example, by preventing hot or cold air from reaching inside, insulation reduces energy consumption in buildings or preserves products’ quality in the transportation and packaging sectors. Proper transportation and storage of temperature-sensitive products such as food or medicine throughout the distribution process are essential for preserving product safety and quality. Temperature is one of the most critical factors for maintaining the quality of such products. Temperature fluctuations can reduce the quality, shorten shelf-life, and spoil perishables in the package during storage and/or transportation because the temperature can activate and accelerate undesired chemical reactions and microorganisms’ growth. Thus, proper thermal insulation shipping/storage boxes are needed as they can protect the packed goods from thermal shocks and heat exchange with the environment and their consequent negative outcomes. Paperboard and polystyrene foam, as the most common traditional commercial packages, are ineffective against thermal fluctuations in transportation packaging due to their narrow thermal insulation as well as poor thermal buffering capacity [1–4]. Hence, new solutions, including packaging materials that can effectively minimize the impact of temperature fluctuations along the product supply/delivery chain, are of great interest. As such, the packaging should be organized to keep the product temperature within desired limits, thereby ensuring the products’ safety, quality, and shelf-life.

Phase change materials (PCMs), also known as latent heat storage materials, can absorb and release a considerable amount of energy as latent heat of phase change by changing from solid to liquid phase and vice versa within a narrow temperature range [5,6]. PCMs can be incorporated with an insulation module to develop a passive temperature control performance package. The designed PCM-based insulations...
can then be employed during the transport, storage, and distribution stages of, for example, canned food, beverages, electronic circuits, as well as pharmaceutical and biomedical products to ensure that the products are in a relatively stable temperature environment [7–9]. PCMs can be classified as inorganics, such as salts and salt hydrates, or organic, like paraffin, fatty acids, and polyethylene glycol (PEG). Among these many PCMs, PEG has attracted wide interest in different fields, from electronic devices and solar thermal systems to automobiles and insulations, due to their favorable intrinsic characteristics such as biocompatibility, nontoxicity, non-corrosiveness as well as affordable large-scale cost perspective [10,11]. Besides, its melting point and enthalpy compatibility, nontoxicity, non-corrosiveness as well as affordable large-

2. Materials and methods

2.1. Materials

Gum Tragacanth (GT) was provided by a local shop while being commercially available as well. It was thoroughly washed with ethanol, dried, and then milled to obtain a fine powder prior to any further use. Polyethylene glycol (PEG 6000) and octadecyl isocyanate (technical grade) were purchased from Sigma-Aldrich. Cloisite Na+ was obtained from BYK Additives (Germany). Ethanol EtaxAa (highly pure ethanol, 99.5 %) was obtained from Alita Industrial (Finland). Biochar was prepared from softwood sawdust via pyrolysis at 700 °C under nitrogen gas in a tube furnace [26]. The carbonized wood sawdust was ground and sieved to a particle size below 50 μm prior to any further use.

2.2. Composite preparation and hydrophobization

A prescribed amount of PEG was dissolved in DI water at 50 °C. A known amount of GT powder was then added to the solution while raising the temperature to 80 °C under continuous stirring. The system was stirred for 24 h to get a clear viscous solution. The final solution was centrifuged at 2000 rpm (Thermo Scientific SL40FR Centrifuge) for 1 h to remove the bubbles and then lyophilized under a vacuum (Christ Alpha 2–4 Freeze Dryer) to get cryogel. The total solid content of both PEG and GT was fixed at 10 wt% in the solution. Three different compositions of each component were prepared, as summarized in Table 1, codded as PCC1 to PCC3. Preliminary testing confirmed PCC3 as the optimal composition regarding mechanical and thermal performances; as such, additives were added to this composition. The samples containing particles (nanoclay or biochar), named PCC3-C and PCC3-B series, were prepared with the same procedure except that, before dissolving PEG, the calculated amount of the particles was dispersed in DI water by 30 min sonication (SSXONIC probe sonicator). The prepa-

In this work, we develop a gum tragacanth-based phase change composite (PCM) with leakage-free thermal regulation properties. To the best of our knowledge, gum tragacanth (GT) has neither been used to stabilize PCMs nor for insulation applications. As a plant-based material, GT is the dried exudates collected from the stems and branches of different species of Astragalus. GT is a heterogeneous and highly branched anionic polysaccharide consisting of water-soluble and water-swellable fragments. The soluble fraction, known as spheroidal, is a mixture of tragacanthic acid and arabinogalactan, while the swellable fraction, bassorin, is a complex of D-galacturonic acid methyl ester units. Fig. S1 shows the chemical structure of GT. Bassorin, constituting a major part of GT, has a high molecular weight (Mw ~ 10^5 Da) and an elongated (rodlike) molecular shape that provides a thick and heavy paste [23–25]. We hypothesized that GT could act as an excellent stabilizer for polar PEG in its melt state due to its molecular structure and hydrophilic characteristics enabled by the numerous hydrophilic functional groups such as hydroxyl and carboxyl. As such, several compositions of GCC insulation material are prepared via simple aqueous-based blending and adjusting the GT and PCM dry mass ratios to balance latent heat storage and insulation properties of the final product. The water resistance of the developed composite is then improved by coating a thin layer of octadecyl isocyanate (ODI), while its mechanical properties and thermal stability are enhanced significantly by adding two cost-effective and environmentally friendly particles, i.e., Cloisite Na+ and biochar (BC). Our PCC insulation material showed the combined advantages of porosity, low density, hydrophobicity, robust mechanical stability, high thermal stability, and excellent thermal inertia, thus opening possibilities for applications in diverse areas, from building to transportation packaging insulation.

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>PEG (wt%)</th>
<th>GT (wt%)</th>
<th>Clay (wt%)</th>
<th>Biochar (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GT</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PCC1</td>
<td>90</td>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PCC2</td>
<td>80</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PCC3</td>
<td>70</td>
<td>30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PCC3-B1</td>
<td>66.5</td>
<td>28.5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>PCC3-B2</td>
<td>63</td>
<td>27</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>PCC3-C1</td>
<td>66.5</td>
<td>28.5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>PCC3-C2</td>
<td>63</td>
<td>27</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>
2.3. Characterization

2.3.1. Porosity

The porosity of the PCCs was measured based on the method reported in our previous work [27]. The cube PCC with specified dimensions was dried at 50 °C in a vacuum oven. It was weighted (m₀) and immersed in ethanol. After 48 h, it was taken out, its excess ethanol was removed with a blotting paper, and weighted again (m₁). The porosity (ϕ) was calculated using Eq. (1), in which V is the apparent volume of the sample and ρ is the ethanol density (789 kg m⁻³). Each measurement was repeated five times, and the mean value ± standard deviation was reported.

\[ \Phi = \frac{m_1 - m_0}{\rho V} \]  

2.3.2. Scanning electron microscopy

The microstructure of the PCCs was monitored with a Zeiss Sigma VP scanning electron microscope. The samples were coated with a thin layer (~ 4 nm) of gold before the subjection of imaging. The pore size dimensions was dried at 50 °C and weighed (m₂). The porosity of the PCCs was measured based on the method reported.

2.3.3. Fourier transform infrared spectroscopy

The chemical structure of the samples was studied on a Fourier transform infrared spectroscopy (FTIR) device (PerkinElmer FTIR with ATR model). The measurement was performed between 4000 cm⁻¹ and 5000 cm⁻¹ with a scan rate of 16 and a resolution of 4 cm⁻¹.

2.3.4. Contact angle measurement

The contact angle of a water droplet was measured on Theta Flex optical tensiometer device at 25 °C. 5 μl water droplet was placed on the sample’s surface, and two digital photographs of the droplet were captured immediately and 120 s after deposition.

2.3.5. Compression test

The compressive mechanical properties of the PCCs were evaluated on Universal Tester Instron 4204 machine. The cylinder-shaped samples were first conditioned for 72 h at temperature and relative humidity of 24 °C and 55 %, respectively. After that, they were subjected to the compressive force of 1 kN with a rate of 1 mm min⁻¹. Compressive modulus (tangent modulus at 1 % strain) and compressive strength at 30 % and 70 % strain were reported and discussed. Each measurement was repeated three times, and the mean value ± standard deviation was reported.

2.3.6. Thermogravimetric analysis

The thermal decomposition trend of the samples was monitored by thermogravimetric analysis (TGA) performed on TA Instruments TGA Q500. The samples were heated up from room temperature to 800 °C with a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere with a flow of 60 mL min⁻¹.

2.3.7. Differential scanning calorimetry

The phase change properties of the PCCs were examined by differential scanning calorimetry (DSC) (TA Instruments Discovery DSC 250 Auto model). The samples were subjected to three heating-cooling cycles from −10 °C to 90 °C with a heating/cooling rate of 5 °C min⁻¹ under a nitrogen atmosphere. The melting temperature (Tm), crystallization temperature (Tc), melting enthalpy (ΔHm), and crystallization enthalpy (ΔHc) were extracted from all cycles, and the mean values ± standard deviation were reported. The heating/cooling cycles were repeated 100 times on the optimum composition to examine the cyclability of phase change behavior.

2.3.8. Thermal conductivity

A TCI Thermal Conductivity Analyzer (C-Therm) using a modified transient plane source (MTPS) technique was used to measure the thermal conductivity of the PCCs. A disk-shaped geometry with a diameter of 30 mm was used.

2.3.9. Thermal chamber and camera

The insulation performance was measured in a thermal chamber under a temperature-controlled program to increase the temperature from room value to 70 °C. The measurement was conducted with water-filled bottles covered with the developed insulations. The thickness of the insulation was 12 mm in all samples. The results were compared with a bare bottle as well as a bottle covered with commercial polyethylene foam with thermal conductivity of 0.040–0.095 W m⁻¹ K⁻¹ and a bulk density of 100 Kg m⁻³ (based on the product data sheet) and a thickness of 12 mm (Fig. S2). Furthermore, a PCC sample was placed on a hot plate, and the temperature distribution images versus time were captured by a FLER SC7000 infrared thermal camera.

3. Results and discussion

3.1. Morphological properties

Highly porous structures with low bulk density have been considered the core material for thermal insulation systems [28,29]. Thus, the porosity and bulk density of the developed PCCs were examined and summarized in Table 2. All samples revealed a relatively low bulk density ranging from 115 to 140 kg m⁻³ and high porosity within 73 to 88 %. Although the density range was higher than that of light foam-based insulation materials, such as expanded polystyrene or polyurethane foam, it was close to the reported values for glass and rock wool as well as plant-based insulations [16,17,19]. In the case of PCC1 to PCC3, the bulk density increased upon increasing the GT content,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (kg m⁻³)</th>
<th>Porosity (%)</th>
<th>Mean pore size (μm)</th>
<th>Thermal conductivity (W m⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC1</td>
<td>113 ± 3</td>
<td>88 ± 3.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PCC2</td>
<td>115 ± 5</td>
<td>85 ± 3.4</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PCC3</td>
<td>119 ± 4</td>
<td>83 ± 3.3</td>
<td>130 ± 40</td>
<td>0.036 ± 0.001</td>
</tr>
<tr>
<td>PCC3-B1</td>
<td>121 ± 5</td>
<td>81 ± 3.1</td>
<td>85 ± 18</td>
<td>0.037 ± 0.002</td>
</tr>
<tr>
<td>PCC3-B2</td>
<td>126 ± 6</td>
<td>74 ± 3.0</td>
<td>28 ± 10</td>
<td>0.038 ± 0.002</td>
</tr>
<tr>
<td>PCC3-C1</td>
<td>124 ± 5</td>
<td>80 ± 2.9</td>
<td>33 ± 10</td>
<td>0.037 ± 0.001</td>
</tr>
<tr>
<td>PCC3-C2</td>
<td>134 ± 7</td>
<td>73 ± 3.0</td>
<td>104 ± 48</td>
<td>0.039 ± 0.001</td>
</tr>
</tbody>
</table>
which could be due to the higher bulk density of the GT powder than that of PEG. The bulk density slightly increased in PCC with the additives, which could be explained by the higher dry mass content. Noticeably, a linear trend was observed between the density and porosity of PCC, where the samples with higher bulk density revealed a lower porosity (Fig. S3), similar to that reported by Trambitski et al. [30].

SEM images in Fig. 2 were captured from the cross-section area of the PCCs to monitor their porosity and pore size. All samples possessed a typical three-dimensional porous architecture with open-cell microstructures, in which the irregular-shaped pores, characterized by interconnectivity and robust internal structure, were distributed evenly throughout the PCCs. The incorporation of BC or Cloisite Na⁺ did not change the pore geometry considerably, yet consistent with the literature [31], the PCC with additives revealed a denser and more uniform microstructure compared with the particle-free samples. The average pore size decreased from 130 ± 40 μm for PCC3 to 28 ± 10 μm for PCC-B2 (Table 2), which could be due to its higher dry mass as well as its highly dense, robust, and well-developed network structures resulting in the creation of pores with smaller sizes [25,32]. Furthermore, no evidence of phase separation was observed in all PCCs, and the particles were distributed homogeneously in most PCCs. Only in the case of PCC3-C2 clay particles showed minor agglomeration, as spherical particles could be seen in the SEM image with a higher magnification (red arrow in Fig. 2f), and as a result, the pore size increased significantly to 104 ± 48 μm.

### 3.2. Chemical structure and surface properties

For the long-term application of thermal insulators, water resistance is essential so that the material can still maintain a low thermal conductivity in a humid environment. Besides, it is essential to deter the destruction of the porous insulation skeleton structure through water vapor absorption by the pores [33,34]. Due to the presence of abundant hydroxyl groups of GT, the hydrophilic nature of GT could be easily altered by using long-chain aliphatic molecules, e.g., ODI. In the current study, the hydrophobic modification was applied by coating the surface of PCCs with a thin layer of ODI molecules. FTIR was carried out to investigate the possible covalent bonding between the hydroxyl groups of the GT and the isocyanate group of ODI. FTIR spectra of the PCC3-B2 and PCC3-C2 before and after surface coating are depicted in Fig. 3a. Except for the hydroxyl groups’ characteristic peak at 3400 cm⁻¹, the other main characteristic peaks were untouched after surface coating with ODI. The considerable reduction in the peak intensity at 3400 cm⁻¹ suggested the consumption of hydroxy groups during the coating process. Besides, some new bands appeared after surface coating. Namely, two pronounced peaks formed at 2910 cm⁻¹ and 2850 cm⁻¹ regions that could be due to asymmetric and symmetric methylene groups in the alkyl chain of the coated ODI. Furthermore, two new bands appeared at 1615 cm⁻¹ and 1580 cm⁻¹, which could be attributed to the amide I and amide II vibration peaks. The FTIR spectra confirm the reaction between isocyanate groups of ODI and hydroxyl groups of GT and PEG. Of note, the proper removal of ODI molecules after the washing was verified by the absence of any characteristic peaks in the region of 2270 cm⁻¹, which is assigned to the isocyanate group [35,36]. According to our previous experiments obtained from the elemental analysis, the amount of grafted ODI is around 10 wt% [35,36].

The FTIR spectra of initial components and PCCs, as well as a thorough peaks description, are provided in the Supplementary Information. All the characteristic peaks of the initial components were observed in the PCCs (Fig. S4), while their intensity slightly changed according to the portion of each component. No new characteristic bands appeared on the spectra of the PCCs, indicating the physical nature of the interactions between PEG and GT.

A water contact angle measurement was carried out further to explore the surface properties, i.e., the surface wettability of the PCCs after ODI coating. A contact angle greater than 90° is considered a hydrophobic solid surface in which the liquid is not easy to wet the solid. Besides, the larger the contact angle, the worse the material surface’s wettability [37]. The photographs of the water droplet immediately and 120 s after deposition are provided in Fig. 3b to Fig. 3e. The contact angle was less than 90° before coating, while it increased to approximately 128° afterward, indicating a notable change in the surface properties. The coating of ODI on the surface of the PCC3-B2 insulation converted the surface from hydrophilic to hydrophobic. The water droplet formed a stable sphere on the surface of the ODI-coated sample, which was well preserved even after 120 s (Fig. 3e). Unlike the coated sample, the water droplet was absorbed in 10 s in the uncoated insulation (Fig. 3c), showing its high hydrophilic surface property. A routine water absorption test was also performed to evaluate the water retention capacity of the PCC3-B2 insulation before and after coating. While the uncoated insulation disintegrated in water within 60 min, the ODI-coated one maintained well even after a week (Fig. 5) with minor water absorption of 3.6 ± 0.3 %. Altogether, the contact angle measurement, along with the water absorption study, confirmed that the ODI coating was favorable for the water resistance performance of the PCCs, which could be due to its low polar long aliphatic chains.

![Fig. 2. SEM images of a) PCC3, b) PCC3-B1, c) PCC3-B2, d) PCC3-C1, and e) and f) PCC3-C2.](image-url)
3.3. Mechanical resilience

For insulating materials, the elastic behavior, reflected by compressive strength and modulus, is of great significance due to its direct effect on the insulating properties [38]. Hence, the compressive properties of the developed PCCs, i.e., the compressive modulus and compressive strength at 30 % and 70 % strain, were examined. The typical compressive stress-strain curves, as well as the comparison of different compressive properties, are depicted in Fig. 4. All formulations had good stability without any visual fracture throughout the test. They presented a linear viscoelastic behavior at low strain rates, afterward a relatively large plateau region, and finally, a densification zone. This trend was consistent with the compression behavior of open-cell porous materials and suggested a flexible deformation pattern of the developed insulations [16,39]. Both compressive modulus and compressive strength increased significantly with increasing GT content. Furthermore, adding the particles, i.e., Cloisite Na\(^+\) and BC, notably improved the compressive properties. For instance, the compressive modulus increased from 5.3 ± 0.4 MPa in PCC1 to 6.6 ± 0.5 MPa in PCC3 and further enhanced to 11.1 ± 0.9 MPa in PCC3-B2. Similarly, the compressive strength at 70 % strain improved from 72 ± 4 kPa in PCC1 to 317 ± 11 kPa and 702 ± 21 kPa in PCC3 and PCC3-B2, respectively. Such improvement in compressive performance could be due to the increase in density and reduction in porosity upon increasing the portion of GT and adding particles. Moreover, it could be attributed to the uniform dispersion of the particles with higher rigidity and their good compatibility with the polymer matrix that strengthen the cell walls and structure [16,39]. The improved network regularity and the degree of crosslinking freedom, and the decrease in the polymer chains’ flexibility could be other reasons to enhance mechanical performance [31,40]. To conclude, the observed compressive properties of the composite insulations in the current study were in good agreement with those reported for bio-based composites containing clay [41,42] or biochar [31,43]. Besides, they were in line with the compressive properties of the expanded polystyrene foam [38,44,45], as well as polyurethane foam [46,47], making them potential candidates for insulated packaging materials.

3.4. Thermogravimetric analysis

The thermal stability of the polymeric composites can be increased by incorporating fillers and additives [48]. The thermal decomposition of PCCs, as well as the initial materials, were monitored by TGA in a nitrogen atmosphere to investigate the effect of additives, i.e., BC and Cloisite Na\(^+\), on the thermal stability of the developed PCCs. The TGA/DTG thermograms are depicted in Fig. 5, and the corresponding data, including the 5 % (T5%), 10 % (T10%), and maximum decomposition temperatures (Tmax), as well as the char residue at 800 °C, are summarized in Table 3. The plain PEG presented one sharp mass loss step that started at approximately 210 °C and ended at about 410 °C with a Tmax of 395 °C, like that reported by Zhao et al. [11] and Wang et al. [49], who used plain PEG with the same molecular weight. GT showed two pronounced mass loss regions, an approximately 10 % mass loss below 200 °C attributed to the release of the hydroxyl groups, followed by a considerable mass loss of approximately 65 % assigned to the
decomposition of the polysaccharide backbone [50]. As expected, PCC presented three mass loss regions, two of which were due to the GT portion and the third to the PEG portion. Furthermore, the intensity of the decomposition DTG peaks changed in proportion to the concentration of the components, i.e., PEG and GT.

Although $T_{\text{max}}$ did not change significantly after the presentation of BC or Cloisite Na$^+$, $T_{5\%}$ and $T_{10\%}$ showed a shift. For instance, $T_{5\%}$ and $T_{10\%}$ increased from 195 °C and 245 °C in the PCC3, respectively, to 245 °C and 260 °C in the PCC composed of 10 wt% BC. The same trend could be seen for the PCC containing Cloisite Na$^+$. These results revealed that the weight losses in the composite insulations started at higher temperatures than the plain PCC3, and adding the particles lowered the decomposition rate and improved the thermal stability. Likewise, the char residue increased considerably in the composites, indicating that the decomposition of polymers was hindered by the particles, and they enhanced the thermal stability [51,52]. As shown in Fig. S6, both BC and Cloisite Na$^+$ had platelet structures; therefore, they could form an effective diffusion barrier, acting as a thermal insulator and shielding combustible products from heat during thermal decomposition [48,53].

The increased heterogeneity of the composite structure compared to the composition with no additives, morphology optimization of char layers, mechanical reinforcement, and preventing or reducing dripping behavior have been reported as other reasons for the observed higher thermal stability in the high aspect ratio particle/polymer blends [54–56]. Overall, both BC and Cloisite Na$^+$ improved the thermal property of the PCCs in terms of the delay of decomposition temperatures and displayed great potential and benefits in preparing high thermal stability materials, as previously reported in other composites [57]. Notably, the BC-incorporated insulation presented higher thermal stability than the clay-incorporated one, which could be explained by the better thermal stability of BC than Cloisite Na$^+$ (Fig. S7). Of note, the slightly lower thermal stability of PCC3-C2 than PCC3-C1 could be explained by the partial aggregation of the clay particles at a high loading of 10 wt% [58,59], as previously proved in SEM images.

3.5. Phase change properties

DSC studies were performed to evaluate the PCCs’ phase change
properties, including melting temperature (T_m), melting enthalpy (ΔH_m), crystallization temperature (T_c), and crystallization enthalpy (ΔH_c), as reported in Table 3 and Fig. 6. Pure PEG showed T_m and T_c at 57.4 °C and 34.5 °C, with 185.2 J g⁻¹ and 176.3 J g⁻¹ melting and crystallization enthalpy values, respectively. Like the plain PEG, the PCCs showed one melting and one crystallization peak. Thus, GT only served as a supporting matrix and did not restrict the normal phase change process of PEG in the composite. Although both T_m and T_c did not change significantly, the corresponding enthalpies were reduced proportionally to the decrease in the PEG portion, likewise with the results reported for PEG-based phase change materials [10,60]. For example, the melting and crystallization enthalpies decreased from 160 J g⁻¹ and 152 J g⁻¹ for the composition with 90 % PEG to 106.9 J g⁻¹ and 104.8 J g⁻¹ for the formulation with 70 % PEG. The lowest enthalpy values were seen for PCC3-C2, which could be attributed to the smaller portion of PEG compared with the rest of the compositions, as well as the binding of intermolecular hydrogen bonds that can prevent the movement of ether chain and crystalline area of the PEG segments [61]. Surprisingly, for the PCC3-B2 and PCC-C1 formulations, the phase change enthalpies were slightly higher than the particle-free sample, i.e., PCC3. These insulations seemed to provide an optimal pore structure that could hold more PEG than the other samples [62]. Furthermore, the DSC of PCC3-B2 before and after ODI coating showed insignificant differences (Fig. S8). Briefly, DSC thermograms supported that the phase change enthalpies of the developed PCCs were promising for creating high-performance PCM systems in the field of thermal management [15].

To investigate the possibility of PEG leakage, the PCC3 and PCC3-B2 insulations were kept in an oven at 80 °C for 2 h and then subjected to DSC testing. The DSC curves are depicted in Fig. 7a. Furthermore, a thermal cycling test, in which the melting and solidification scans were repeated 100 times, was performed to study the phase transition stability of the PCC3-B2 insulation. The 1st and 100th cycles are provided in Fig. 7b, and the whole heating-cooling cycles are depicted in Fig. S9. Moreover, the measured phase change properties before and after the cycling test are tabulated in Table 4. It is obvious that the phase transition enthalpy did not show a noticeable change after heat treatment at 80 °C, indicating there was no leakage or loss of the PCM [63]. In other words, PEG was effectively kept in the porous structure of the GT matrix. The absence of the PEG leakage could also be observed from the photographs captured from the insulations before and after heat treatment at 80 °C (Fig. 7c and Fig. S10). On the other side, the DSC curve of the PCC3-B2 insulation did not change after the heating/cooling cycles. Compared to the 1st cycle, after the 100th cycle, the enthalpies just slightly decreased; namely, a 5.7 % decrease in the enthalpy of melting and the 3.3 % decrease in the crystallization enthalpy. These small reductions could be due to the increasing nonactive PCM caused by intermolecular interactions that become more profound by the continuous rapid temperature change [64,65]. The FT-IR spectra of the PCC3-B2 before and after cycling are compared in Fig. S11 to provide more evidence for stability. As can be seen, no considerable difference could be detected between the spectra before and after cycling, indicating no PEG leakage and significant stability of the developed PCM insulation even after 100 times cooling/heating cycles. All in all, the developed PCM not only presented phase transition stability but also possessed excellent cycle stability, ensuring the ability to adjust the road temperature over a lengthy period of time.

### 3.6. Thermal insulation performance

The thermal insulation performance of the composite insulations was tested with a water bottle covered with a 12 mm insulation layer, as depicted in Fig. 8b. The changes in water temperature inside the bottle were investigated in a thermal chamber upon heating from room temperature to 70 °C and a consequent cooling back to room temperature. The results are plotted in Fig. 8a. As can be seen, the bare bottle temperature rose continuously and reached the maximum value of 68 °C in 45 min. However, the temperature increased at a lower rate in the
covered bottles, and the maximum temperature was considerably lower. For instance, it was 50 °C in the bottle covered with commercial PE foam and 44 °C in the bottles covered with our PCC insulations. The results strongly showed the benefit of insulations, especially the developed ones in the current study, enabling consistent prevention of thermal shocks or transients arising from sudden temperature changes in the surrounding environment. Similar performance was previously observed with cellulosic PCM composites [64]. It is worth mentioning that the high thermal insulation properties of the PCCs were consistent with their low thermal conductivity values, which ranged from 0.035 to 0.038 W m⁻¹ K⁻¹ (Table 2). Biopolymeric foams and aerogels are known for their low thermal conductivity within the 0.020 and 0.040 W m⁻¹ K⁻¹ range [66,67]. Nevertheless, by comparing the thermal conductivity of the composite insulations with the commercial PE, it could be found that the higher performance of the developed insulations was not only due to their low thermal conductivity but also attributed to the incorporation of PEG, acting as an energy-storage material. To conclude, our lightweight composite insulations could be considered promising alternatives for fossil-based insulations in eco-friendly and energy-efficient applications, thanks to the low conductivity of the biopolymer (GT) and the high thermal inertia of the PCM (PEG).

The temperature distribution images of the PCC sample placed on a hot plate are given in Fig. 8d and Fig. S12. It can be observed that heat was transferred very slowly within the material, even when it was placed in direct contact with a hot object. This is consistent with the thermal conductivity values and the water bottle test. After removing the heating source, the middle of the sample could hold the absorbed heat (Fig. S12).

4. Conclusions

In this study, we developed a series of bio-based insulation materials consisting of gum tragacanth (GT) biopolymer and polyethylene glycol (PEG) phase change material (PCM). Additionally, biochar (BC) and Cloisite Na⁺ additives were incorporated to enhance their mechanical strength and thermal stability. The phase change composite (PCC) was then covered with a thin layer of octadecyl isocyanate (ODI) to alter its surface properties from hydrophilic to hydrophobic. The PCCs possessed a low-density porous structure (up to 88 %) with very low thermal conductivity (0.035 W K⁻¹ m⁻¹). Furthermore, the formulations composed of BC and Cloisite Na⁺ revealed robust mechanical stability under compression, as well as good thermal stability. After ODI coating, the wettability and water uptake capacity of the composite was minor, demonstrated by the water droplet contact angle and water impression test. The PCCs provided leakage-free phase transition enthalpy up to 160 J g⁻¹ and excellent cycling stability, ensuring the ability to adjust road temperature over a long period. Overall, our PCC provides all the

<table>
<thead>
<tr>
<th>Sample’s condition</th>
<th>Tm (°C)</th>
<th>ΔHm (J g⁻¹)</th>
<th>ΔHc (J g⁻¹)</th>
<th>TC (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before thermal treatment</td>
<td>54.1</td>
<td>112.1</td>
<td>107.3</td>
<td>39.3</td>
</tr>
<tr>
<td>After thermal treatment</td>
<td>56.4</td>
<td>108.3</td>
<td>105.2</td>
<td>39.2</td>
</tr>
<tr>
<td>1st heating-cooling cycle</td>
<td>55.3</td>
<td>111.3</td>
<td>106.8</td>
<td>39.2</td>
</tr>
<tr>
<td>100th heating-cooling cycle</td>
<td>60.7</td>
<td>104.9</td>
<td>103.2</td>
<td>40.8</td>
</tr>
</tbody>
</table>

a The data extracted from the first heating/cooling cycle.
necessary properties of excellent insulation, such as high porosity, low density, hydrophobicity, robust and mechanical stability, as well as thermal inertia and enthalpy of PCM. These make PCC an excellent candidate for many temperature- and energy-sensitive applications, including insulation packaging materials.

CRediT authorship contribution statement

Hossein Baniasadi: Conceptualization, Investigation, Methodology, Formal analysis, Visualization, Writing – original draft. Jukka Seppälä: Resources, Writing – review & editing, Funding acquisition. Ari Kankunen: Methodology, Writing – review & editing. Maryam Roza Yazdani: Conceptualization, Investigation, Methodology, Formal analysis, Visualization, Resources, Writing – original draft, Funding acquisition.

Declaration of competing interest

The authors declare that there is no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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