

Smart Bioinsulating Composites for Thermal Comfort and Energy Efficiency

C. Delgado-Sánchez, A. Tenorio-Alfonso, F. J. Navarro and P. Partal

Pro²TecS-Chemical Process and Product Technology Research Center
Department of Chemical Engineering, Physical Chemistry and Material Sciences
ETSI, Universidad de Huelva,
Campus El Carmen 21071 Huelva (Spain)

Abstract. This work aims to develop an efficient technology for valorizing by-products from agricultural and forestry activities by creating high-performance thermal insulators. Complex biodispersions were designed by incorporating phase change materials (PCM) into biofoams for thermal storage and regulation applications. The developed composites demonstrated effective PCM encapsulation, with latent heat storage capacities reaching up to 96.58 J/g for the highest PCM concentration studied. These materials will enhance industrial efficiency in areas such as high-temperature heat recovery, cold energy storage, and building insulation. Additionally, this material not only seeks technological advancement in insulation, crucial for conserving energy by minimizing thermal transfer and improving the safety and quality of industrial processes, but it also stands out as a sustainable technology. The use of bio-based polymers also maximises biomass resources and generating socio-economic benefits through employment in agriculture and forestry.

Key words. Thermal insulation, bio dispersions, phase change materials (PCM), thermal energy storage, sustainable technology.

1. Introduction

The depletion of fossil fuel sources, the rising demand for energy, and environmental concerns such as climate change and pollution highlight the urgency of developing sustainable materials and technologies. Energy conservation and efficiency are essential strategies, alongside renewable energy production, to promote resource sustainability.

A key area of interest is the development of multifunctional materials from natural and renewable sources for energy applications. The building sector, which is responsible for nearly 40% of total energy consumption, is a primary focus for energy-saving strategies. For example, the European Union has set a target to reduce energy use for building climate control by 50% by 2050 [1]. Similarly, industrial applications, such as refrigeration facilities, thermal management in electronics, and waste heat recovery systems, require innovative materials capable of mitigating significant temperature gradients and optimizing energy efficiency.

One promising approach to improving energy efficiency is thermal energy storage, particularly through latent heat storage using phase change materials (PCMs). PCMs can store and release large amounts of energy at almost constant temperatures, making them interesting and highly efficient for thermal regulation. Their integration into building materials or industrial systems enables passive thermal control, reducing energy demands associated with heating and cooling processes. In this context, PCMs contribute to thermoregulation mechanisms that enhance the thermal properties of construction and insulation materials [2]. Despite these advantages, practical application is often hindered by issues such as phase separation, leakage during phase transitions, and low thermal conductivity. To overcome these challenges, various encapsulation and composite strategies have been developed to stabilize PCMs within porous matrices, enhancing both their durability and thermal performance [3].

Another effective strategy to reduce energy consumption is the development of high-performance insulation materials. Traditional options, such as polyurethane and polystyrene foams, offer low thermal conductivity but raise environmental concerns due to their non-biodegradability and high production footprint. As a result, there is growing interest in bio-based insulating foams derived from agroforestry and lignocellulosic materials, such as tannins, lignin, cellulose, and hemicellulose [4]. These materials provide a more sustainable alternative while maintaining effective insulation performance, making them suitable for applications in construction, cold-chain logistics, and industrial thermal management.

Despite these advancements, an optimal strategy for integrating PCMs into biofoams while maintaining structural stability and thermal efficiency remains an open challenge. This study presents a novel approach by combining biofoams with PCMs to develop smart insulating composites with improved thermal performance. The study focuses on optimizing the formulation and processing of thermal biofoams made from plant by-products, establishing an effective protocol for incorporating PCMs into the precursor foam mixture

through emulsification. The work evaluates the impact of PCM content on the morphology, thermal properties, and structural characteristics of the resulting composites, offering key insights into their viability for energy-efficient applications.

2. Methodology

The smart bio-insulating material was developed using tannin supplied by Lupla S.A. (Spain) as the lignocellulosic component and paraffin wax (58–60°C, purchased from PANREAC QUIMICA S.L.U., Spain) as the PCM. The preparation of the tannin-based structure followed the protocol described in Szczurek et al.'s research work [5], where an aqueous tannin solution polymerizes in presence of sodium silicate (Na_2SiO_3) (Fig. 1).

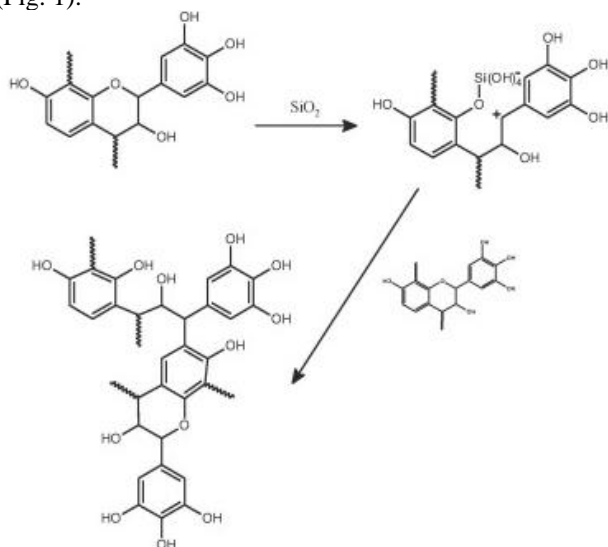


Fig. 1. Suggested mechanism of the SiO_2 -catalysed auto condensation of tannin [5].

For the preparation of PCM-incorporated samples, paraffin wax was introduced at different concentrations (5, 17.2, and 25 wt.% relative to the total wet weight of the sample, prior to drying) by forming a stable emulsion previous to polymerization. This process involved heating the paraffin above its melting temperature and emulsifying it into the tannin aqueous phase using a surfactant under high-shear conditions to ensure uniform dispersion. Once a stable emulsion was achieved, sodium silicate was added as a catalyst to initiate polymerization, forming a rigid tannin-based network that effectively captured the PCM. The resulting composites were subsequently dried under controlled conditions to complete the crosslinking process and enhance structural stability. The specific amounts of each component used in the formulations are detailed in Table 1.

The morphology of the emulsions obtained before crosslinking was analysed using an optical microscope (Olympus System Microscope BX52, Japan), fitted with a light polarizer and an Olympus Digital Camera C5050Z. The emulsion was examined both above and below the melting temperature of the paraffin wax. For low-temperature analysis, cross-polarized light was used to observe the paraffin crystals. Once the catalyst was added and polymerization occurred, the resulting smart

biocomposites were characterized by several techniques to evaluate their structural and thermal properties. Thermal properties are particularly important for evaluating the energy storage and thermal regulation capabilities of the composites. Differential scanning calorimetry (DSC) was used to study the phase change behavior of the materials. Samples were heated and cooled between 100 and -80°C at a rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen flow. The key thermal parameters, including melting and crystallization temperatures, as well as the corresponding enthalpies, were determined from the thermograms, providing insights into the material's thermal efficiency and phase change behavior.

Table 1. – Composition of the bioinsulating foams with different PCM contents before drying.

Samples	Tannin aqueous solution (g)	Surfactant (g)	Catalyst (g)	Paraffin Wax (g)
Biocomposite	20	1	3	0
B1	20	1	3	1
B5	20	1	3	5
B8	20	1	3	8

3. Results and discussion

The successful preparation of the PCM in tannin-aqueous emulsions was confirmed through optical microscopy analysis. Fig. 2 shows the micrographs of the precursor emulsion of sample B5 at 80°C , above the melting point of paraffin, and at 20°C , after cooling, highlighting the changes in the morphology as the paraffin solidifies.

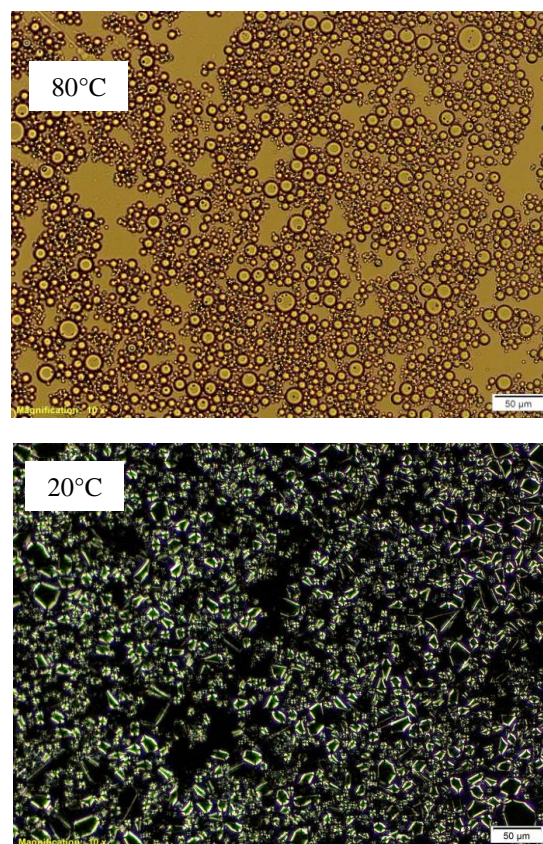


Fig. 2. Precursor emulsion of sample B5: upper image at 80°C (above paraffin melting point), lower image at 20°C (after cooling) under cross-polarized light.

At high temperature, the dispersed paraffin phase appeared as uniformly distributed droplets within the aqueous tannin solution, indicating efficient emulsification. Upon cooling, cross-polarized light microscopy revealed the formation of bright crystalline structures. The crystallized phase exhibited a polyhedral morphology, with independent, well-defined particles, while maintaining the overall homogeneity of the emulsion. The formation of these non-spherical paraffin crystals during the cooling of paraffin-based emulsions has also been reported by other authors [6]. These observations suggest that the emulsification process effectively stabilized the PCM phase, ensuring uniform dispersion before polymerization.

Following the addition of the catalyst, polymerization proceeded successfully, leading to the formation of stable biocomposites capable of integrating the PCM while maintaining structural integrity. As shown in Fig. 3, the freshly prepared smart bioinsulating material exhibited a homogeneous and uniform appearance, indicative of an effective crosslinking process. The observed morphology suggests that the emulsification and polymerization steps facilitated the encapsulation of the PCM within the tannin-based matrix, minimizing phase separation and preventing leakage. The final stage of controlled drying further enhanced the stability of the network, ensuring the material retained its structural cohesion and intended thermal functionality.



Fig. 3. Smart biocomposite just after processing.

The thermal behavior of the smart biocomposites was evaluated using DSC analysis (Fig. 4), comparing the response of the main components with that of the biocomposites, both with and without PCM. The results confirm that the PCM retained its characteristic phase transition properties within the biopolymer matrix, effectively storing and releasing latent heat within the expected temperature range. The thermal events corresponding to melting and crystallization remained well-defined, indicating that the integration process did not alter the PCM's functionality.

Table 2 presents the phase change parameters of pure paraffin wax and the developed smart biocomposites with different PCM contents. The phase change parameters studied include melting and crystallization peak

temperatures (T_{mpeak} , T_{cpeak}) and phase change enthalpies (ΔH_m , ΔH_c). As expected, the data reveal a clear correlation between PCM content and latent heat storage capacity, with higher PCM concentrations leading to increased enthalpy values. Moreover, no significant shifts in transition temperatures were observed, suggesting that the bio-based matrix provided an effective encapsulation environment without interfering with the thermal behavior of the PCM.

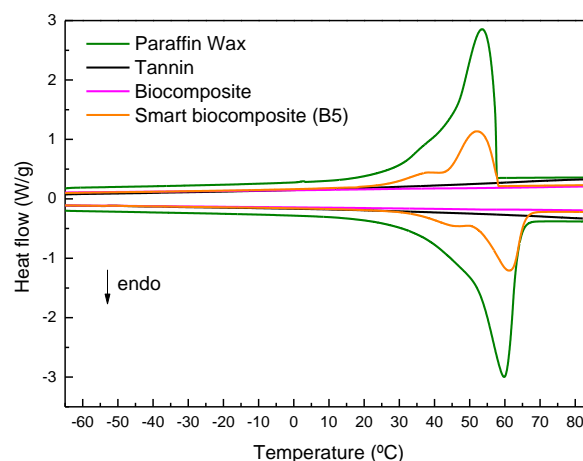


Fig. 4. DSC measurements of pure components, the biocomposite without PCM and with PCM (smart biocomposite, B5).

The ability of these composites to undergo repeatable phase transitions while maintaining thermal stability is a key factor in their potential application for energy-saving insulation. The combination of bio-based foams with PCMs enables passive temperature regulation, reducing fluctuations and enhancing energy efficiency in building and industrial applications. Additionally, the stabilization of the PCM within the tannin-based matrix minimizes leakage risks, improving long-term performance and durability.

Table 2. – Phase change parameters of pure PCM and the smart biocomposites with different PCM contents.

Samples	T_{mpeak} (°C)	ΔH_m (J/g)	T_{cpeak} (°C)	ΔH_c (J/g)
Paraffin Wax	59.82	207.18	53.49	205.42
B1	59.72	29.01	52.92	28.60
B5	60.66	76.49	51.07	75.79
B8	60.14	96.58	51.36	95.96

When compared to other construction materials incorporating paraffin-based PCMs, the developed smart biocomposites initially demonstrate competitive thermal performance. For instance, gypsum boards with 44.5 wt.% paraffin exhibit a crystallization enthalpy (ΔH_c) of 40.30 J/g [7], while plaster containing 35.71 wt.% paraffin reaches 28.50 J/g [8]. In contrast, the B5 smart biocomposite with 17.2 wt.% paraffin in its wet state—corresponding to approximately 44 wt.% after drying—achieves a ΔH_c of 75.8 J/g, indicating a significantly higher energy storage capacity per unit mass of material. These results confirm that the bio-based matrix efficiently encapsulates the PCM, preserving its phase

change properties and highlight its potential for energy-efficient management, though further studies on thermal conductivity and long-term stability are needed for optimization.

4. Conclusion

This research has made significant progress in developing a highly interesting smart bio-insulating composite by combining agricultural and forestry by-products with PCMs. Specifically, this study successfully integrated paraffin wax as PCM within tannin-based foams, demonstrating its potential for thermal insulation and energy storage. The optimized emulsification and polymerization process enabled effective PCM encapsulation, ensuring structural integrity and minimizing leakage. The thermal characterization confirmed that the composites retained the PCM's phase transition properties, with latent heat storage capacities reaching up to 96.58 J/g for the highest PCM concentration studied.

This innovative composite represents a promising starting point for further exploration, offering both thermal insulation and energy storage capabilities. Compared to conventional insulation materials, the incorporation of PCMs enhances thermal regulation, reducing temperature fluctuations and contributing to energy savings in building and industrial applications. While the results are encouraging, further optimization is required to improve properties such as thermal conductivity, mechanical strength, and PCM incorporation methods, including gelation pathways.

This study lays a strong foundation for next-generation sustainable thermal management materials, providing a scalable and eco-friendly alternative for enhancing energy efficiency in construction and industrial sectors. Future research should focus on refining PCM incorporation techniques and assessing large-scale applicability to maximize their real-world impact.

Acknowledgements

This work is part of the project PID2023-149701OA-I00 and TED2021-131284 B-I00 funded by MCIN/AEI/10.13039/501100011033 (Spanish Ministry of Science, Innovation and Universities) and ERDF "A way of making Europe". This research was also funded by the project EPIT1162023 (University of Huelva, Spain).

C. Delgado-Sánchez acknowledges financial support from the EMERGIA research program (DGP_EMEC_2023_00091) from Consejería de Universidad, Investigación e Innovación (Junta de Andalucía).

References

- [1] D. Ürgen-Vorsatz, L. F. Cabeza, S. Serrano, C. Barreneche, K. Petrichenko, (2015) «Heating and cooling energy trends and drivers in buildings», *Renew. Sustain. Energy Rev.*, vol. 41, pp. 85-98.
- [2] L. F. Cabeza, (2021) «Components. Thermal Energy Storage», in *Reference Module in Earth Systems and Environmental Sciences*, Elsevier.
- [3] Y. Zhang, Z. Jia, A. Moqet Hai, S. Zhang, B. Tang, (2022) «Shape-stabilization micromechanisms of form-stable phase change materials-A review», *Compos. Part Appl. Sci. Manuf.*, vol. 160, p. 107047.
- [4] C. Delgado-Sánchez, F. Santiago-Medina, V. Fierro, A. Pizzi, A. Celzard, (2018) «Optimisation of "green" tannin-furanic foams for thermal insulation by experimental design», *Mater. Des.*, vol. 139, pp. 7-15.
- [5] A. Szczurek, V. Fierro, G. Medjahdi, A. Celzard, (2019) «Carbon aerogels prepared by autocondensation of flavonoid tannin», *Carbon Resour. Convers.*, vol. 2, n.o 1, pp. 72-84.
- [6] C. Liu, Z. Zheng, C. Xi, Y. Liu, (2021) «Exploration of the natural waxes-tuned crystallization behavior, droplet shape and rheology properties of O/W emulsions», *J. Colloid Interface Sci.*, vol. 587, pp. 417-428, abr. 2021,
- [7] A. Oliver Ramírez, F. J. Neila González, A. García Santos, (2011) «Incorporación de los materiales de cambio de fase en placas de yeso para almacenamiento de energía térmica mediante calor latente": caracterización térmica del material mediante la técnica DSC», *Inf. Construcción*, vol. 63, n.o 522, Art. n.o 522.
- [8] M. Karkri, M. Lachheb, F. Albouchi, S. B. Nasrallah, I. Krupa, (2015) «Thermal properties of smart microencapsulated paraffin/plaster composites for the thermal regulation of buildings», *Energy Build.*, vol. 88, pp. 183-192.