

Research Article

Leakage-Free Wood-Derived Activated Carbon/Methyl Palmitate Composite Phase Change Material for Thermal Management Applications

Gökhan Hekimoğlu

Karadeniz Technical University, Department of Metallurgical and Material Engineering, 61080 Trabzon, Turkey. (e-mail: ghekimoğlu@ktu.edu.tr).

ARTICLE INFO

Received: May., 06. 2023

Revised: Oct., 03. 2023

Accepted: Nov., 01. 2023

Keywords:

Phase change materials

Composites

Thermal energy storage

Latent heat

Activated Carbon

Corresponding author: Gökhan Hekimoğlu

ISSN: 2536-5010 / e-ISSN: 2536-5134

DOI: <https://doi.org/10.36222/ejt.1293404>

ABSTRACT

This study aimed to create a leakage-free composite phase change material (PCM) that has high potential for various thermal management applications. Activated carbon derived from wood (ACW) with a porous structure was used to address the leakage issue and improve the thermal conductivity of Methyl palmitate (MPt) used as the PCM. The optimum MPt impregnation ratio was found to be 53 wt% in the leakage-free ACW/MPt composite. The results of FTIR analysis showed that the integration of MPt and ACW was achieved through physical interaction. Scanning electron microscopy (SEM) analysis indicated that MPt was uniformly distributed within pores of the ACW scaffold. DSC analyses demonstrated that the fusion enthalpy and temperature of the ACW/MPt (53 wt%) were 129 J/g and 27.59 °C, respectively. Thermal gravimetric analysis (TGA) measurements confirmed that the ACW/MPt was thermally stable. By incorporating MPt with ACW, thermal conductivity of MPt was increased by 2.16 times. The fusion enthalpy of ACW/MPt did not change, and the melting temperature remained constant after 750 thermal cycles. The results of this study indicate that the fabricated leak-free ACW/MPt is cost-effective and environmentally friendly and has the potential to be utilized as a thermal energy storage (TES) material for temperature regulation in various applications.

1. INTRODUCTION

With the ever-increasing demand for thermal management systems due to increasing energy cost and decreasing the traditional energy sources, there is a need for more efficient and reliable methods for controlling temperature, particularly in buildings with the highest energy consumption rates [1]. One of the most favorable technologies for thermal management is the use of phase change materials (PCMs) that can store and release thermal energy during phase transition [2]. However, traditional PCMs have some drawbacks, such as low thermal conductivity and potential leakage while melting [3,4]. Therefore, there is a need for the development of new PCM-based composites with enhanced properties. Form-stable composite PCMs (FSC-PCMs) have emerged as a promising alternative to traditional PCMs. FSC-PCMs are materials that combine a PCM with a supporting material, such as clay-based materials, polymers, biochar or activated carbon [5,6]. The properties of FSC-PCMs can be tailored depending on the features of the selected supporting material and PCM. For example, the type of PCM and supporting material, the composition of components, the production route and the

particle size of the components can all affect the thermal properties of the FSC-PCMs. By optimizing these parameters, it is possible to develop FSC-PCMs with specific thermal properties to suit different applications [7,8]. Therefore, the resulting FSC-PCMs materials have improved shape-stability and thermal conductivity, making them suitable for various applications, including building insulation, electronics cooling, temperature management of batteries, transportation of food or medical products, textile products, etc [9-12].

Activated carbon (AC) is an ideal supporting material for creation FSC-PCMs due to its high surface area, porous structure, and thermal stability. The AC provides a large surface area and porous structure for the PCM to be adsorbed, thereby preventing leakage and improving shape-stability. Furthermore, relatively high thermal conductivity of AC allows for efficient heat transfer between PCMs and the surrounding environment. Therefore, recently many researches focused on the fabrication and application of FSC-PCMs comprising of AC and PCM for thermal management systems [13-15].

Gu et al [16] assessed the use of carbonized pepper straws as a carrier material to load palmitic acid and found that this composite had a fusion enthalpy of 95.50 J/g. Zhang et al. [17]

created a FSC-PCM of a fatty acid eutectic mix utilizing bio-carbon from waste corn. This composite, which contained about 78% PCMs, reached a fusion enthalpy of 148.30 J/g and an 87.5% improvement in thermal conductivity. Xu et al. [18] combined paraffin with carbonized orange peels, resulting in a leakage-free composite with high thermal stability. Wen et al. [19] proposed FSC-PCM using sunflower straw-based carbon loaded with melted stearic acid for TES applications.

In the current study, a novel FSC-PCM was developed by impregnating Methyl palmitate (MPt) selected as PCM into the pores of AC-derived from wood (ACW), which served as an effective framework. Wood is an important source of carbon due to its low cost and easy availability [20,21]. To date, there have been no investigations on the fabrication and extensive investigations of such a leak-resistant ACW/MPt composite in the literature. The composite's crystalline/chemical structures and surface morphology were analyzed using XRD, FTIR and SEM techniques. DSC and TGA analyses were conducted to evaluate the composite's TES potential, while its thermal reliability and conductivity were also measured. Overall, these analytical techniques provided comprehensive insights into the properties of the samples and facilitated a detailed assessment of their suitability for TES applications. The results indicated that the favorable energy storage capacity and thermal conductivity of this FSC-PCM make it a promising material for thermoregulation applications in different thermal management systems.

2. EXPERIMENTAL

2.1. Material

Methyl palmitate (MPt, assay 99%) was purchased from Sigma Aldrich Company, while ACW was provided from Rota Chemical Company (surface area: 1150 m²/g, density: 0.25-035 g/cm³, pore volume: 1.3 ml/g).

2.2. Preparation of leakage-free ACW/MPt composite

The leakage-free ACW/MPt composite was prepared using the sorption method with vacuum operation. Optimal impregnation conditions were achieved through a vacuum operation in a vacuum oven maintained at 80 kPa and 50 °C for a duration of 3 hours, facilitating the infiltration of liquid MPt into the ACW pores. To determine the maximum MPt loading capacity of ACW, various amounts (ranging from 30 to 70 wt%) of MPt was impregnated into its porous network. To avoid clumping of the ACW/MPt mixtures, the samples were periodically taken out of the oven and stirred every 30 minutes, ensuring an even infiltration of MPt throughout the ACW matrix. The form-stability of each fabricated composite was assessed through leakage tests. For this, each composite was heated on filter paper above the melting point of MPt. The sample that demonstrated the highest MPt rate without leaching out after heating for 2 h was identified as FSC-PCM. The leakage-free ACW/MPt was found to have a MPt ratio of 53 wt% and ACW ratio of 47 wt%, as depicted in the given test results in Fig. 1.

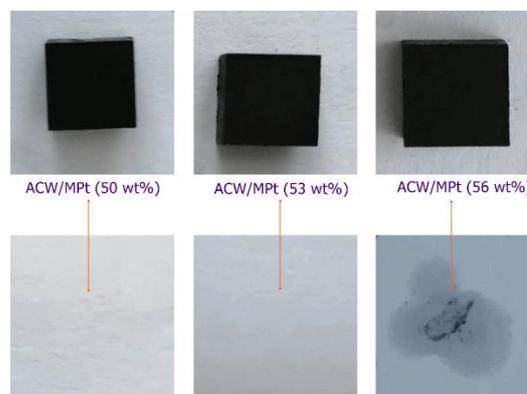


Figure 1. The leakage test result of ACW/MPt samples

2.2. Characterization

In this study, a range of experimental techniques were applied to reveal the micro-structure, chemical structure, TES properties, and thermal stability of ACW, MPt, and resulting ACW/MPt specimens. FTIR (Shimadzu, IRSpirit), DSC (Hitachi 7020), SEM (Zeiss LEO 440) and TGA (PerkinElmer) analyses were utilized to examine the samples. The thermal cyclers device (Prime3Techne) was conducted to assess the cycling stability of the ACW/MPt. The thermal conductivity of the specimens were measured using a thermal conductivity meter (Decagon KD2 Pro).

3. RESULTS

3.1. SEM Results

SEM images in Fig. 2 illustrate the morphology of pure ACW and the ACW/MPt samples prepared in the study. The SEM image of pure ACW reveals the presence of numerous pores, predominantly micro-sized, which is consistent with its high PCM loading capacity findings. These pores provide abundant space for loading MPt and were successfully occupied by the MPt, indicating good physical compatibility between the ACW and MPt. Additionally, ACW/MPt composite exhibited a uniform distribution of MPt embedded within the porous network structure of ACW. Consequently, the pores of ACW were compacted with the loadage of MPt, leading to a relatively smooth surface. Overall, the results suggest that the MPt was effectively integrated with ACW.

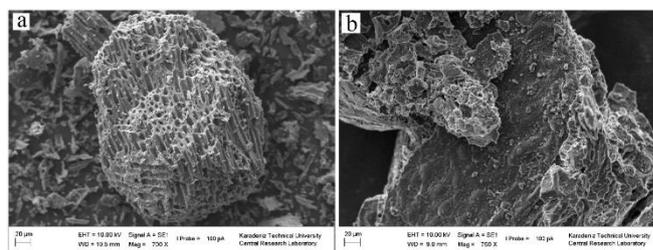


Figure 2. SEM images of ACW (a) and ACW/MPt (b)

3.2. FTIR Results

The FTIR spectra of MPt, ACW and ACW/MPt were demonstrated in Figure 3. The spectrum of MPt exhibited peaks at 2910 and 2857 cm⁻¹, which corresponded to CH₂ group stretching vibrations. Additionally, peaks at 1734 and 1169 cm⁻¹

¹ were observed, which were attributed to the carbonyl groups and the stretching vibrations of C-O-C, respectively. Peaks at 1460, 885, and 716 cm^{-1} were representative of the vibrations of the -OH functional group. The FTIR spectra of ACW was found to be similar with general carbon-based materials, with absorption bands between 1924 and 2285 cm^{-1} . Notably, the impregnation of MPt into ACW resulted in negligible changes in the position and intensity of the peaks, indicating that the MPt retained its phase change and chemical properties in the composite structure without the formation of new peaks.

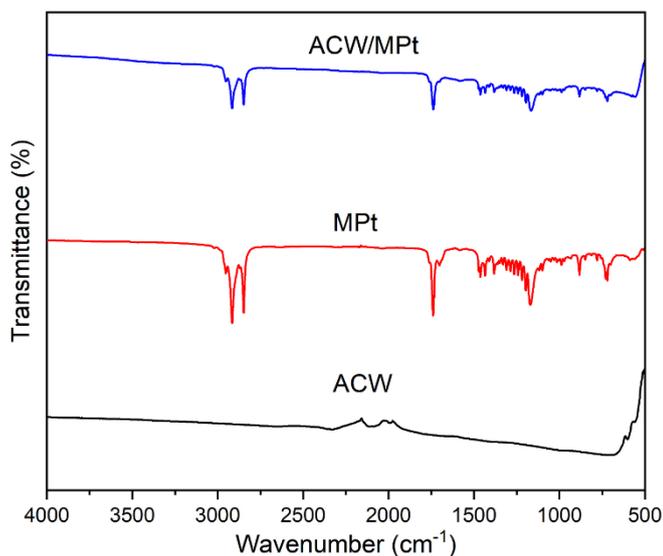


Figure 3. FTIR spectra of MPt, ACW and ACW/MPt

3.3. DSC Results

Figure 4 shows the DSC thermograms for MPt and ACW/MPt, while Table 1 presents the TES data for these materials. Three measurements were conducted for each sample to calculate the mean deviations. The results indicated that the mean deviations in phase transition temperatures and enthalpy values were ± 0.17 °C and $\pm 0.82\%$ J/g, respectively. The pure MPt has melting and freezing temperatures of 26.97 and 25.15°C, respectively, and its fusion and freezing latent heats are 245 and -242 J/g, respectively. The melting/freezing temperatures of ACW/MPt composite only changed slightly, with measurements of 27.59/26.27°C. The measured latent heats of ACW/MPt are 129/-127 J/g, respectively. The high surface area and porous structure of ACW led to higher latent heat capacity of ACW/MPt composite. The fusion and freezing enthalpy of ACW/MPt is about 52.65% and 52.47% of the pure MPt, respectively, which aligns with the impregnation ratios of MPt. Furthermore, the DSC thermogram for ACW/MPt is similar to that of MPt, indicating that MPt maintains its TES role throughout the phase changes.

It is worth noting that the fusion enthalpy of the leakage-free ACW/MPt composite is comparable to that of different bio-carbon-based FSC-PCM reported in the literature [14,16,22-24]. More specifically, the fusion enthalpy of the mentioned leakage-free AC-based composites was reported as 87.42, 95.5, 84.74, 108.0, and 90.2 J/g, respectively. When considering the measured fusion heat of 129 J/g for the suggested ACW/MPt composite, it is highly competitive.

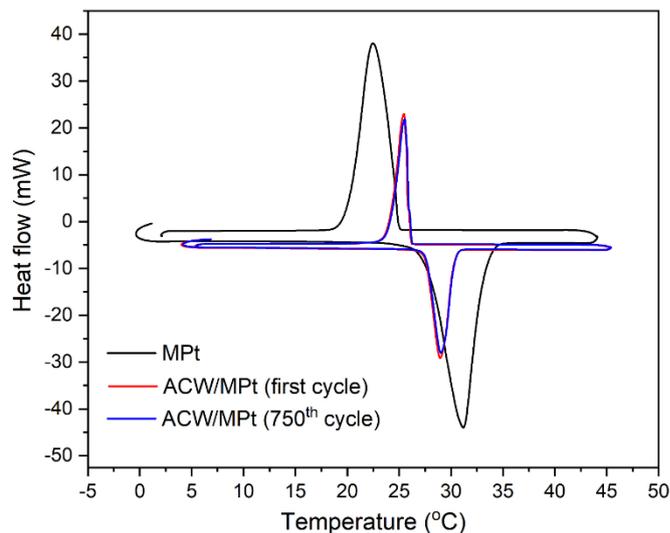


Figure 4. DSC thermograms of MPt and ACW/MPt

To assess the cycling thermal stability of the leakage-free ACW/MPt, a thermal cycle test was conducted by subjecting it to 750 melting/freezing cycles. The DSC curves for this composite before and after 750 thermal cycles are presented in Fig. 4. The DSC results revealed that its melting/freezing temperatures and enthalpy values hardly changed. These findings infer the cycling stability of ACW/MPt, which is critical for TES applications.

TABLE I

Sample	DSC DATA OF MPt AND ACW/MPt			
	Melting Temperature (°C)	Fusion Enthalpy (J/g)	Freezing Temperature (°C)	Freezing Enthalpy (J/g)
MPt	26.97	245	25.15	-242
ACW/MPt	27.59	129	26.27	-127
ACW/MPt (750 th cycle)	27.55	128	26.25	-127

3.4. TGA Results

The TGA curves in Figure 5 depict the thermal stability of ACW, MPt and ACW/MPt. The results demonstrate that MPt remained stable up to a temperature of 174 °C, after which it experienced substantial decomposition. ACW exhibited good thermal stability, with no signs of major decomposition, except for minor weight loss due to the evaporation of water and volatile organic substances. It experienced weight loss of 8.07% at 500 °C. Furthermore, the TGA curve of ACW/MPt not only determined its thermal stability, but also verified the amount of MPt present into ACW. It experienced similar rapid mass losses with pure MPt. Mass losses due to MPt in ACW/MPt occurred between 174 and 228 °C, and its corresponding mass losses were approximately 60%, which closely aligns with MPt impregnation rate and ACW-based mass losses. Overall, the decomposition temperature of ACW/MPt was significantly higher than its working temperature, indicating its high resistance to thermal degradation. In light of these findings, it can be concluded that ACW/MPt possess considerable strength against thermal degradation.

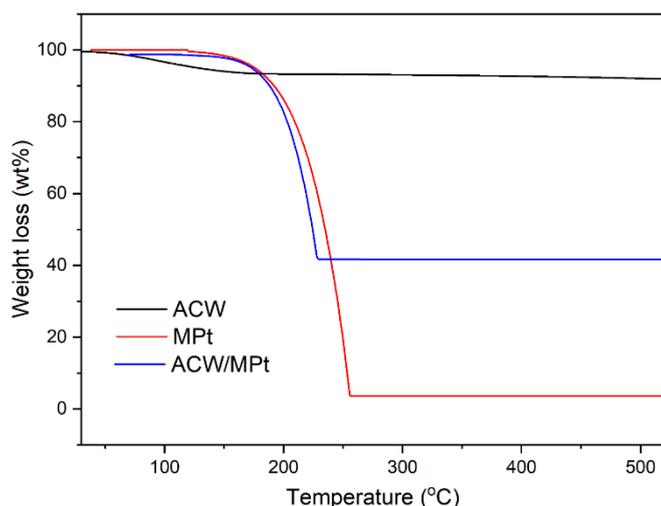


Figure 5. TGA curves of MPt, ACW and ACW/MPt

3.5. Thermal Conductivity Results

Thermal conductivity (TC) is a key factor that significantly affects the period of heat charging/discharging of PCM-based systems. The TC values of pure MPt, ACW, and the ACW/MPt were measured at 0.24, 0.33, and 0.52 W/m.K, respectively, at a temperature of 20 °C. Based on this finding, the TC of the ACW/MPt composite was 2.16 times higher than that of MPt, owing to the carbon skeleton of ACW that provides heat transfer channels and heat conduction framework. However, the TC of the ACW/MPt composite was found to be slightly higher than expected, compared to that of ACW and MPt. Although the TC of ACW is not high enough to theoretically supply this increase in the TC of MPt, it boosted significantly its TC. This is since the majority of the air molecules in the pores of ACW, which have much lower TC (0.025 W/m.K), were displaced by the MPt. As a result, the TC of ACW/MPt could be higher than that of either the MPt or ACW alone. Therefore, the used ACW not only provided form-stability for MPt as a supporter matrix, but also acted as a doping agent, significantly enhancing the low TC of MPt. These findings were also reported in previous studies [15,25,26].

4. CONCLUSION

This study utilized highly porous activated carbon derived from wood (ACW) to create novel leakage-free FSC-PCM for thermal energy storage (TES). Methyl palmitate (MPt) was successfully impregnated into the porous structure of ACW. The loading rate of MPt in the leakage-free ACW/MPt was 53 wt%. The fusion enthalpy of ACW/MPt was 129 J/g with a melting temperature of 27.59 °C. The composite had high thermal stability up to 174 °C, and admirable cycling stability even after 750 melting-freezing cycles. The thermal conductivity of ACW/MPt was 2.16 times higher than that of the pure MPt. Overall, the used ACW not only allowed for high loading of MPt, but also significantly enhanced the thermal conductivity of MPt without the need for additional fillers. As a result, the leak-free ACW/MPt composite has high potential for various TES applications including solar passive thermal management of buildings, cooling of electronic devices/batteries and textile products etc.

ACKNOWLEDGEMENT

Dr. G. Hekimoğlu thanks the KTU due to the instrumentation facilities.

REFERENCES

- [1] F. Kuznik et al., "A review on phase change materials integrated in building walls", *Renewable and Sustainable Energy Reviews*, vol. 15, no. 1, pp. 379–391, 2011, doi: 10.1016/j.rser.2010.08.019i.
- [2] I. Sarbu and C. Sebarchievici, "A Comprehensive Review of Thermal Energy Storage," *Sustainability*, vol. 10, no. 1, p. 191, Jan. 2018, doi: 10.3390/SU10010191.
- [3] A. Sharma, V. V. Tyagi, C. R. Chen, and D. Buddhi, "Review on thermal energy storage with phase change materials and applications," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 2, pp. 318–345, Feb. 2009, doi: 10.1016/J.RSER.2007.10.005.
- [4] S. Wu, T. Yan, Z. Kuai, and W. Pan, "Thermal conductivity enhancement on phase change materials for thermal energy storage: A review," *Energy Storage Mater.*, vol. 25, pp. 251–295, Mar. 2020, doi: 10.1016/j.enstm.2019.10.010.
- [5] Y. Zhang, Z. Jia, A. Moqet Hai, S. Zhang, and B. Tang, "Shape-stabilization micromechanisms of form-stable phase change materials-A review," *Compos Part A Appl Sci Manuf*, vol. 160, p. 107047, Sep. 2022, doi: 10.1016/j.compositesa.2022.107047.
- [6] P. Lv, C. Liu, and Z. Rao, "Review on clay mineral-based form-stable phase change materials: Preparation, characterization and applications," *Renewable and Sustainable Energy Reviews*, vol. 68, pp. 707–726, Feb. 2017, doi: 10.1016/j.rser.2016.10.014.
- [7] M. M. Kenisarin and K. M. Kenisarina, "Form-stable phase change materials for thermal energy storage," *Renewable and Sustainable Energy Reviews*, vol. 16, no. 4, pp. 1999–2040, May 2012, doi: 10.1016/j.rser.2012.01.015.
- [8] J. Paul et al., "Nano-enhanced organic form stable PCMs for medium temperature solar thermal energy harvesting: Recent progresses, challenges, and opportunities," *Renewable and Sustainable Energy Reviews*, vol. 161, p. 112321, Jun. 2022, doi: 10.1016/J.RSER.2022.112321.
- [9] S. Rostami et al., "A review of melting and freezing processes of PCM/nano-PCM and their application in energy storage," *Energy*, vol. 211, p. 118698, Nov. 2020, doi: 10.1016/J.ENERGY.2020.118698.
- [10] X. Huang, C. Zhu, Y. Lin, and G. Fang, "Thermal properties and applications of microencapsulated PCM for thermal energy storage: A review," *Appl Therm Eng.*, vol. 147, pp. 841–855, Jan. 2019, doi: 10.1016/J.APPLTHERMALENG.2018.11.007.
- [11] P. K. S. Rathore and S. kumar Shukla, "Improvement in thermal properties of PCM/Expanded vermiculite/expanded graphite shape stabilized composite PCM for building energy applications," *Renew Energy*, vol. 176, pp. 295–304, Oct. 2021, doi: 10.1016/j.renene.2021.05.068.
- [12] L. Yang, J. Huang, and F. Zhou, "Thermophysical properties and applications of nano-enhanced PCMs: An update review," *Energy Convers Manag.*, vol. 214, p. 112876, Jun. 2020, doi: 10.1016/j.enconman.2020.112876.
- [13] D. G. Atinafu, B. Y. Yun, S. Wi, Y. Kang, and S. Kim, "A comparative analysis of biochar, activated carbon, expanded graphite, and multi-walled carbon nanotubes with respect to PCM loading and energy-storage capacities," *Environ Res.*, vol. 195, no. February, p. 110853, 2021, doi: 10.1016/j.envres.2021.110853.
- [14] A. F. Nicholas, M. Z. Hussein, Z. Zainal, and T. Khadiran, "Palm kernel shell activated carbon as an inorganic framework for shape-stabilized phase change material," *Nanomaterials*, 2018, doi: 10.3390/nano8090689.
- [15] G. Hekimoğlu, A. Sari, Y. Önal, O. Gencel, V. V. Tyagi, and E. Aslan, "Utilization of waste apricot kernel shell derived-activated carbon as carrier framework for effective shape-stabilization and thermal conductivity enhancement of organic phase change materials used for thermal energy storage," *Powder Technol.*, vol. 401, p. 117291, Mar. 2022, doi: 10.1016/J.POWTEC.2022.117291.
- [16] X. Gu, P. Liu, C. Liu, L. Peng, and H. He, "A novel form-stable phase change material of palmitic acid-carbonized pepper straw for thermal energy storage," *Mater Lett*, 2019, doi: 10.1016/j.matlet.2019.03.130.

- [17] W. Zhang et al., "Lauric-stearic acid eutectic mixture/carbonized biomass waste corn cob composite phase change materials: Preparation and thermal characterization," *Thermochim Acta*, vol. 674, pp. 21–27, Apr. 2019, doi: 10.1016/J.TCA.2019.01.022.
- [18] Y. Xu et al., "Preparation and performance of shape-stable phase change materials based on carbonized-abandoned orange peel and paraffin," vol. 27, no. 4, pp. 289–298, Apr. 2019, doi: 10.1080/1536383X.2018.1543279.
- [19] R. Wen, W. Zhang, Z. Lv, Z. Huang, and W. Gao, "A novel composite Phase change material of Stearic Acid/Carbonized sunflower straw for thermal energy storage," *Mater Lett*, 2018, doi: 10.1016/j.matlet.2017.12.008.
- [20] H. Yang et al., "Low-cost, three-dimension, high thermal conductivity, carbonized wood-based composite phase change materials for thermal energy storage," *Energy*, vol. 159, pp. 929–936, Sep. 2018, doi: 10.1016/J.ENERGY.2018.06.207.
- [21] Z. Yang, Y. Deng, and J. Li, "Preparation of porous carbonized woods impregnated with lauric acid as shape-stable composite phase change materials," *Appl Therm Eng*, 2019, doi: 10.1016/j.applthermaleng.2019.01.063.
- [22] Y. Wan et al., "A promising form-stable phase change material prepared using cost effective pinecone biochar as the matrix of palmitic acid for thermal energy storage," *Sci Rep*, vol. 9, no. 1, p. 11535, Dec. 2019, doi: 10.1038/s41598-019-47877-z.
- [23] G. Hekimoğlu et al., "Walnut shell derived bio-carbon/methyl palmitate as novel composite phase change material with enhanced thermal energy storage properties," *J Energy Storage*, vol. 35, p. 102288, Mar. 2021, doi: 10.1016/j.est.2021.102288.
- [24] L. Feng, J. Zheng, H. Yang, Y. Guo, W. Li, and X. Li, "Preparation and characterization of polyethylene glycol/active carbon composites as shape-stabilized phase change materials," *Sol Energy Mater Sol Cells*, vol. 95, no. 2, pp. 644-650, Feb. 2011, doi: 10.1016/j.solmat.2010.09.033.
- [25] G. Hekimoğlu, A. Sarı, S. Arunachalam, H. Arslanoğlu, and O. Gencil, "Porous biochar/heptadecane composite phase change material with leak-proof, high thermal energy storage capacity and enhanced thermal conductivity," *Powder Technol*, vol. 394, pp. 1017–1025, Dec. 2021, doi: 10.1016/j.powtec.2021.09.030.
- [26] L. Feng, J. Zheng, H. Yang, Y. Guo, W. Li, and X. Li, "Cost-Effective Biochar Produced from Agricultural Residues and Its Application for Preparation of High Performance Form-Stable Phase Change Material via Simple Method," *Int J Mol Sci*, vol. 19, no. 10, p. 3055, Oct. 2018, doi: 10.3390/ijms19103055

BIOGRAPHIES

Gökhan Hekimoğlu obtained his BSc degree in Metallurgical and Material Engineering Department from Karadeniz Technical University (KTU) in 2012. He received his MSc. diploma in Material Science from the University of Manchester in England in 2016, and PhD degree in Graduate School of Science, Metallurgical and Material Engineering Department from Karadeniz Technical University in 2022. His research interests are heat storage materials, form stable composite phase change materials and thermal management systems. Since 2017 he has been working as a research assistant in Metallurgical and Material Engineering Department in KTU.