

# Bio-Based Polymers for Environmentally Friendly Phase Change Materials

Subjects: Materials Science, Composites

Contributor: Kinga Pielichowska, Katarzyna Nowicka-Dunal, Krzysztof Pielichowski

Phase change materials (PCMs) have received increasing attention in recent years as they enable the storage of thermal energy in the form of sensible and latent heat, and they are used in advanced technical solutions for the conservation of sustainable and waste energy. Importantly, most of the currently applied PCMs are produced from non-renewable sources and their carbon footprint is associated with some environmental impact. However, novel PCMs can also be designed and fabricated using green materials without or with a slight impact on the environment.

Keywords: phase-change materials ; bio-based polymers ; thermal energy storage ; shape stabilization

---

## 1. Introduction

Phase-change materials (PCMs) are an important class of thermoresponsive materials used for the storage of thermal energy as sensible and latent heat. The application of PCMs in energy-related technical solutions can substantially impact the efficient use and conservation of sustainable and waste energy. Thermal energy storage in the form of latent heat provides a large density of energy storage with small temperature fluctuations during heat storage and release. As PCMs, different types of materials have been investigated including salts, salt hydrates, paraffins, and fatty acids, as well as polymeric materials usually characterized by solid–solid or solid–liquid phase transition <sup>[1][2][3]</sup>. They are usually modified with different materials to obtain shape-stabilized PCMs, encapsulated PCMs, or to improve some properties, e.g., thermal conductivity.

Most of the currently applied PCMs are obtained from non-renewable sources and their environmental impact is connected with a certain carbon footprint. However, novel PCMs can also be designed and fabricated using green materials without or with a slight impact on the environment.

Polymers are used in PCMs in different aspects, e.g., as PCMs themselves, for PCMs' shape stabilization, or microencapsulation, but also as precursors in the carbonization process to obtain porous carbon materials that can be then applied for the shape stabilization of PCMs. Representative examples are poly(ethylene glycol) that is widely used as a polymeric PCM, and phenol formaldehyde and melamine formaldehyde resins, polyester, and acrylate resins that are widely applied for the microencapsulation of paraffin or fatty-acid-based PCMs <sup>[4]</sup>. On the other hand, for the shape stabilization of PCMs polyurethanes and polyethylene are utilized <sup>[5]</sup>.

To decrease the negative impact of PCMs on the natural environment and carbon footprint, there is a search for “green” solutions. One of the potential routes is the application of bio-based polymeric materials in the broad areas of PCMs and thermal energy storage by replacing (at least partially) synthetic polymers with bio-based ones <sup>[6][7][8]</sup>. Following this route it is possible to minimize PCMs environmental impact and carbon footprint in various sectors, such as building and energy sectors.

## 2. Bio-Based Polymers

According to the definition, bio-based polymers are polymers obtained from renewable resources, mostly from biomass <sup>[9]</sup>. At the end of the 20th century, the polymer industry was confronted with global warming, as well as the depletion of crude oil and petroleum-based products. Nowadays, bio-based polymers are a subject of intensive research, as they can play a crucial role in decreasing the carbon dioxide emissions causing global warming and using limited fossil resources <sup>[10]</sup>. One of the possible solutions of these problems was to use sustainable resources and materials instead of components derived from fossil resources <sup>[11][12]</sup>. The natural source of raw materials is biomass, and agricultural waste from, e.g., corn or potatoes could be a feedstock for numerous bio-based polymers <sup>[13]</sup>.

However, in recent years, numerous research and industrial efforts have been made to develop new biotechnology and green chemical processes in order to preserve land devoted for food production.

Bio-based polymers can be divided in three main groups:

- First class—polymers prepared from biomass, such as starch, cellulose, chitosan, chitin, sodium alginate, and natural rubber, including those polymers which are chemically modified;
- Second class—polymers obtained using microorganisms and plants, e.g., poly(hydroxyalkanoates) and poly(glutamic acid);
- Third class—synthetic polymers obtained from naturally derived monomers from renewable resources, e.g., bio-polyolefins, polylactide, poly(lactide-co-glycolide), poly(butylene succinate), bio-poly(ethylene glycol) PEG, bio-poly(ethylene terephthalate) [9][11][14].

Polymer materials based on renewable feedstocks are already being considered as carbon-neutral alternatives to fossil-based polymers, and renewable energy production plays a more and more important role in modern electricity systems.

### **3. Bio-Based Polymers as Phase-Change Materials**

Different types of polymers able to achieve a high degree of crystallinity can be applied as PCMs. Polymers that are commercially available and produced using synthetic routes, which can also be obtained as bio-based polymers, have been described. In polymers, the key issue determining the temperature and heat of phase transition is the degree of crystallinity, which suggests that promising candidates for PCM will be polymers composed of linear macrochains, as well as those in which intermolecular forces enhance the arrangement of crystalline structures. In these polymers which could also be renewably sourced, crystallization occurs relatively easily and leads to the formation of regular crystalline forms. Hence, Kamimoto et al. [15] investigated the possibility of using high-density polyethylene (HDPE) as a PCM. HDPE melts at a temperature of 125–135 °C with a melting heat of up to 240 J/g. An additional advantage of using HDPE as a PCM is the possibility of crosslinking it; and then at the melting temperature of linear HDPE, a solid–solid transition of the crosslinked polymer is observed, associated with changes in macromolecular arrangement. Moreover, HDPE crosslinking (using physical or chemical methods) makes it possible to maintain shape stability at temperatures above the melting point.

Another polymer considered as PCM was trans-1,4-polybutadiene (PB), which, depending on the temperature, occurs in two crystalline forms [16]. The solid–solid phase transition was detected at 78.1 °C, and the heat of this transformation was 144 J/g. Notably, PB melting occurs at a much higher temperature of 140 °C.

A promising group of macromolecular compounds to be applied as PCMs are those based on polyethers, especially polyethylene oxide (PEO). Aliphatic polyethers, also known as poly(alkylene oxides) or poly(alkylene glycols) (when the macromolecules are terminated with an –OH group) or polyalkyl oxides, are a group of polymers with a general formula –O–R–, where R consists of at least two methylene groups, formed by the ring-opening ionic polymerization of oxiranes and using initiating compounds containing an active hydrogen atom [17]. The most important representatives of aliphatic polyethers are PEO, poly(propylene oxide) (PPO), and polytetrahydrofuran (PTHF) [18][19].

Poly(trimethylene oxide) (PTMO) with three methylene units between ether oxygen atoms has a melting point ca. 35 °C, while polytetrahydrofuran with four methylene units between ether oxygen atoms shows a melting temperature ca. 60 °C. In aliphatic polyethers with an increasing number of methylene groups between ether oxygen atoms, the melting point rises to the value of ca. 130 °C, characteristic for linear polyethylene. All unsubstituted poly(alkylene oxides) are highly crystalline, with a degree of crystallinity, even up to 95% for PEO, but the presence of a side chain in the polyether chain causes in extreme cases a completely amorphous structure. PEO is soluble in water and polar organic solvents, and the chemical properties of polyethers are determined by the presence of ether bonds and hydroxyl end groups. Hydroxyl end groups undergo all reactions characteristic of alcohols, while ether bonds are highly resistant to hydrolysis [18][20].

### **4. PCMs Encapsulation Using Bio-Based Polymers**

In most applications, PCMs with a solid–liquid phase transition cannot be directly used due to the leakage above their melting point. Among the most common and effective methods to avoid the leakage, as well as to enhance other properties (such as mechanical ones), is encapsulation; in this process, PCM is sealed by selected tough materials that additionally allow for the enhancement of some PCM properties. The encapsulated PCMs usually consist of a polymer

shell and core (the PCM itself). As a shell material, one can also use organic, inorganic, or hybrid organic–inorganic materials. The shell material selection should take into account its compatibility with PCM but can also aim at improving selected properties, e.g., dimensional stability or thermal conductivity [21][22].

Among synthetic polymer-based shell materials, melamine-formaldehyde (MF) resin, poly(urea-urethane) (PUU), polyurea (PU), urea-formaldehyde (UF) resin, acrylic, resins and polystyrene are vastly used. However, numerous bio-based polymers have been used as shell materials for PCMs, including gum Arabic, chitosan/gelatin, and agar/gelatin/gum Arabic compositions [22].

Hence, Deveci and Basal [23] prepared microcapsules with an n-eicosane core as a PCM and silk fibroin (SF) and chitosan (CS) as a shell material by the complex coacervation method. Sphere-shaped microcapsules were successfully obtained, and the EDS analysis confirmed the effective incorporation of n-eicosane in the microcapsules. The microcapsules obtained at an SF/CS ratio of 5 possessed a dense and nonporous wall, while for the ratio of 20 an inner layer with a smoother surface and a rough outer surface with a spongelike structure were observed. It has also been found that the microencapsulation efficiency affected the n-eicosane content in such a way that a high n-eicosane content improved the microencapsulation efficiency, especially at higher SF/CS ratios.

In another development, PCM microcapsules based on n-nonadecane as the core material and sodium alginate (SA) as the shell material were fabricated by Moghaddam et al. [6] using a melt coaxial electrospray. It has been observed that the microcapsule size was increased with the SA concentration, while smaller microcapsule diameters and a more homogenous dimensional distribution were found for SA concentrations of 1.5% (w/v). A decrease in the needle-to-collector distance from 20 to 5 cm caused mean microcapsule size decrease from 480 to 275  $\mu\text{m}$ . A further reduction in the working distance up to 3 cm allowed them to obtain spherically shaped microcapsules with diameters lower than 100  $\mu\text{m}$ . The obtained results confirmed that for microcapsules with diameters smaller than 100  $\mu\text{m}$ , the n-nonadecane encapsulation ratio was  $56 \pm 5\%$ .

## **5. PCMs Shape Stabilization Using Bio-Based Polymers**

Another method to avoid the leakage of PCMs above their melting temperature is shape stabilization, usually by using porous materials. The shape-stabilization method with porous lightweight materials can limit PCM leakage during the phase transition, but can also improve selected properties such as the thermal conductivity [24].

PEO blends with selected polymers of natural origin or their derivatives—cellulose, cellulose acetate, cellulose ether, carboxymethoxycellulose, and potato starch—were obtained and characterized by the DSC and IR techniques. It has been shown that the phase transformations of the solid–solid type occur in PEO/natural polymer systems and, in the case of selected blends (PEO/cellulose acetate 1:1 w/w and PEO/CMC 1:1 w/w), a synergistic effect appears; however, the obtained systems are characterized by a relatively low phase-transition heat. The shape-stabilization effect was attributed to intermolecular hydrogen interactions between ether oxygen in PEO chains and cellulose (or its derivative) hydroxyl groups, or PEO hydroxyl end groups and oxygen atoms in cellulose macrochains [7][25].

A eutectic mixture of TD and MA was incorporated into hydroxylpropyl methyl cellulose (HPMC) by Qu et al. [26]. The obtained results confirmed that a TD–MA eutectic mixture was distributed uniformly in HPMC, and a form-stable PCMs were obtained. Leakage tests revealed that the absorption efficiency of TD-MA by HPMC was nearly 50%. The thermal properties investigations showed that the temperatures of melting and freezing were 34.61 and 31.09  $^{\circ}\text{C}$ , and the heat of phase transition was 102.11 and 84.58 J/g, respectively. Importantly, the TD-MA/HPMC exhibited a good thermal stability and reliability performance.

PEG-based PCMs shape-stabilized by chitin nanofibers (CNFs) were obtained by Wijesena et al. [27]. Fibrous chitin from crab shells was characterized by a diameter of several tens of nanometers and lengths of up to few micrometers. The best system remained opaque (transmittance  $\sim 3.5\%$ ) below the melting temperature of PEG, while above the melting temperature it was transparent with a transmittance value of  $\sim 88\%$ .

Pinto and co-workers [28] prepared shape-stabilized PCMs based on bacterial cellulose nanofibers (BC) with reduced and non-reduced graphene oxide (GO) and microencapsulated paraffin as PCMs in the foam-like form. They revealed that the presence of GO enhanced the fire-retardancy and dimensional stability of the obtained system.

## 6. Conclusions

Bio-based polymers are currently considered as future candidates for the design and manufacturing of modern phase-change materials. The application of bio-based polymeric materials allows us to minimize PCMs' environmental impact and carbon footprint, especially in the energy- and materials-consuming building and energy sectors. Even a partial replacement of synthetic polymers with bio-based ones makes it possible to decrease the negative impact of PCMs on the natural environment and carbon footprint. In the former area, to avoid leakage, as well as to protect and enhance PCM properties, various encapsulation strategies have been developed, and the most up-to-date trend is the use of bio-based components in the (micro)capsules preparation process. It has been found that the application of bio-based polymers, for instance cellulose and its derivatives, enables the fabrication of encapsulated PCMs with good thermoregulation abilities and acceptable mechanical properties. Interestingly, microencapsulated PCMs composed of gelatin/gum Arabic (polymer shell), and sugarcane wax–Al<sub>2</sub>O<sub>3</sub> composite (core material) have already been tested in solar panels, and a desired reduction in the front-facing glass temperature was observed. In the second area, i.e., PCMs shape stabilization, bio-based polymers are applied to limit PCM leakage during the phase transition, but can also improve selected properties, such as thermal conductivity, as well as shape stability which is of primary importance. In synthetic/natural polymer blends, e.g., PEO/cellulose (derivatives), intermolecular hydrogen interactions between oxygen atoms in PEO chains and hydroxyl groups in cellulose chains (or its derivatives), or hydroxyl end groups in PEO chains and oxygen atoms in cellulose chains, were found to improve the shape stabilization effect. On the other hand, the physical modification of PCMs has also been performed to impart new features to the shape-stabilized systems; e.g., the incorporation of graphene oxide remarkably improved the fire-retardancy of bacterial cellulose-based PCM. In another development, PCMs modified by multi-walled carbon nanotubes were found to provide an advantageous light-to-thermal conversion performance.

To conclude, bio-based polymers are a vast group of materials that can be applied in the design and manufacturing of environmentally friendly phase-change materials with a reduced carbon footprint. Biopolymers can be chemically or physically modified to give them new features, and such new (composite) materials will gradually replace components produced from non-renewable sources and thus contribute to the development of a future advanced 'green' economy.

---

## References

1. Pielichowska, K.; Pielichowski, K. Phase Change Materials for Thermal Energy Storage. *Prog. Mater. Sci.* 2014, 65, 67–123.
2. Zalba, B.; Marin, J.M.; Cabeza, L.F.; Mehling, H. Review on Thermal Energy Storage with Phase Change: Materials, Heat Transfer Analysis and Applications. *Appl. Therm. Eng.* 2003, 23, 251–283.
3. Pielichowska, K.; Pielichowski, K. (Eds.) Multifunctional Phase Change Materials; Elsevier: Amsterdam, The Netherlands, 2023; ISBN 9780323857192.
4. Confalonieri, C.; Gariboldi, E. 9—Shape-Stabilized and Form-Stable PCMs. In *Multifunctional Phase Change Materials*; Pielichowska, K., Pielichowski, K., Eds.; Woodhead Publishing: Southton, UK, 2023; pp. 369–410. ISBN 978-0-323-85719-2.
5. Pielichowska, K.; Bieda, J.; Szatkowski, P. Polyurethane/Graphite Nano-Platelet Composites for Thermal Energy Storage. *Renew. Energy* 2016, 91, 456–465.
6. Moghaddam, M.K.; Mortazavi, S.M.; Khayamian, T. Preparation of Calcium Alginate Microcapsules Containing N-Nonadecane by a Melt Coaxial Electrospray Method. *J. Electrostat.* 2015, 73, 56–64.
7. Pielichowska, K.; Pielichowski, K. Novel Biodegradable Form Stable Phase Change Materials: Blends of Poly(Ethylene Oxide) and Gelatinized Potato Starch. *J. Appl. Polym. Sci.* 2010, 116, 1725–1731.
8. Okogeri, O.; Stathopoulos, V.N. What about Greener Phase Change Materials? A Review on Biobased Phase Change Materials for Thermal Energy Storage Applications. *Int. J. Thermofluids* 2021, 10, 100081.
9. Masutani, K.; Kimura, Y. Biobased Polymers BT—Encyclopedia of Polymeric Nanomaterials; Kobayashi, S., Müllen, K., Eds.; Springer: Berlin/Heidelberg, Germany, 2021; pp. 1–7. ISBN 978-3-642-36199-9.
10. Piorkowska, E. Overview of Biobased Polymers. In *Thermal Properties of Bio-Based Polymers*; Di Lorenzo, M.L., Androsch, R., Eds.; Springer International Publishing: Cham, Switzerland, 2019; pp. 1–35. ISBN 978-3-030-39962-7.
11. Nakajima, H.; Dijkstra, P.; Loos, K. The Recent Developments in Biobased Polymers toward General and Engineering Applications: Polymers That Are Upgraded from Biodegradable Polymers, Analogous to Petroleum-Derived Polymers, and Newly Developed. *Polymers* 2017, 9, 523.

12. Narayan, R. Preparation of Bio-Based Polymers for Materials Applications. *Appl. Biochem. Biotechnol.* 1988, 17, 7–22.
13. Carafa, R.N.; Foucher, D.A.; Sacripante, G.G. Biobased Polymers from Lignocellulosic Sources. *Green Chem. Lett. Rev.* 2023, 16, 2153087.
14. Kimura, Y. Molecular, Structural, and Material Design of Bio-Based Polymers. *Polym. J.* 2009, 41, 797–807.
15. Kamimoto, M.; Abe, Y.; Sawata, S.; Tani, T.; Ozawa, T. Latent Thermal Storage Unit Using Form-Stable High Density Polyethylene; Part I: Performance of the Storage Unit. *J. Sol. Energy Eng.* 1986, 108, 282–289.
16. Iwamoto, Y.; Ikai, S. New Polymeric Material for Latent Heat Thermal Energy Storage. In *Proceedings of the 5th Workshop of the IEA ECES IA Annex 10*, Tsu, Japan, 10 November 2000.
17. Herzberger, J.; Niederer, K.; Pohlit, H.; Seiwert, J.; Worm, M.; Wurm, F.R.; Frey, H. Polymerization of Ethylene Oxide, Propylene Oxide, and Other Alkylene Oxides: Synthesis, Novel Polymer Architectures, and Bioconjugation. *Chem. Rev.* 2016, 116, 2170–2243.
18. Bailey, F.E.; Koleske, J.V. *Poly(Ethylene Oxide)*; Academic Press: Cambridge, MA, USA, 1976; ISBN 9780120732500.
19. Pielichowski, K.; Flejtuch, K. Differential Scanning Calorimetry Study of Blends of Poly(Ethylene Glycol) with Selected Fatty Acids. *Macromol. Mater. Eng.* 2003, 288, 259–264.
20. Flejtuch, K. *Badanie Przemian Fazowych Wybranych Układów Polieterów Pod Kątem Akumulacji Energii Ciepłej*. PhD Thesis, Cracow University of Technology, Krakow, Poland, 2004.
21. Huang, Y.; Stonehouse, A.; Abeykoon, C. Encapsulation Methods for Phase Change Materials—A Critical Review. *Int. J. Heat Mass Transf.* 2023, 200, 123458.
22. Ghasemi, K.; Tasnim, S.; Mahmud, S. PCM, Nano/Microencapsulation and Slurries: A Review of Fundamentals, Categories, Fabrication, Numerical Models and Applications. *Sustain. Energy Technol. Assess.* 2022, 52, 102084.
23. Deveci, S.S.; Basal, G. Preparation of PCM Microcapsules by Complex Coacervation of Silk Fibroin and Chitosan. *Colloid Polym. Sci.* 2009, 287, 1455–1467.
24. Jeon, I.K.; Azzam, A.; Al Jebaei, H.; Kim, Y.-R.; Aryal, A.; Baltazar, J.-C. Effects of Shape-Stabilized Phase Change Materials in Cementitious Composites on Thermal-Mechanical Properties and Economic Benefits. *Appl. Therm. Eng.* 2023, 219, 119444.
25. Pielichowska, K.; Pielichowski, K. Biodegradable PEO/Cellulose-Based Solid-Solid Phase Change Materials. *Polym. Adv. Technol.* 2011, 22, 1633–1641.
26. Qu, M.; Guo, C.; Li, L.; Zhang, X. Preparation and Investigation on Tetradecanol and Myristic Acid/Cellulose Form-Stable Phase Change Material. *J. Therm. Anal. Calorim.* 2017, 130, 781–790.
27. Wijesena, R.N.; Tissera, N.D.; Rathnayaka, V.W.S.G.; Rajapakse, H.D.; de Silva, R.M.; de Silva, K.M.N. Shape-Stabilization of Polyethylene Glycol Phase Change Materials with Chitin Nanofibers for Applications in “Smart” Windows. *Carbohydr. Polym.* 2020, 237, 116132.
28. Pinto, S.C.; Silva, N.H.C.S.; Pinto, R.J.B.; Freire, C.S.R.; Duarte, I.; Vicente, R.; Vesenjak, M.; Marques, P.A.A.P. Multifunctional Hybrid Structures Made of Open-Cell Aluminum Foam Impregnated with Cellulose/Graphene Nanocomposites. *Carbohydr. Polym.* 2020, 238, 116197.

---

Retrieved from <https://encyclopedia.pub/entry/history/show/123653>