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REVIEW ARTICLE

A Systematic Review on Bio-Based Phase Change Materials

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ABSTRACT - Global warming and energy depletion are the main problems faced in recent years due to energy consumption by industries and the global population. Phase change materials (PCMs) with significant properties tend to store and release energy and fill the demand and supply gap. Most organic and inorganic PCMs are not considered environmentally eco-friendly when used for thermal energy storage (TES). Because they are formed from non-conventional energy resources, their carbon footmark and environmental effect are not ignored. To reduce problems, an urgent need for eco-friendly materials is required. Green substitute bio-based phase change materials (BPCMs) have gained extensive attention and are considered the best suitable replacement for organic and inorganic PCMs because BPCMs exhibit significant properties that are cost-effective, eco-friendly, renewable and convenient for thermal energy storage. However, the thermal conductivity of BPCMs is too low, which delays TES and heat transfer rates. Furthermore, this paper summarizes the reduction of low thermal conductivity problems with the help of highly conductive nanoparticles dispersed into the BPCMs and the fabrication methods of BPCMs composites. This article also provides information for futuristic researchers about the methods of fabrication and factors for enhancing the thermal conductivity of an eco-friendly BPCM composite and draws an important conclusion from the literature.

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1.0 INTRODUCTION

Population growth is increasing rapidly, and energy needs have become a severe issue. Thermal energy storage (TES) tends to improve energy requirements across several thermal segments by determining a mismatch between energy requirement and demand [1], [2]. Using phase change material (PCM), TES has established an outstanding courtesy over decades [3]. So, many researchers have the enthusiasm to find the best suitable energy medium for (TES) to fulfil supply demand and reduce the use of non-conventional energy [4]–[6]**.** Latent heat storage has received more attention than sensible heat storage because of its low cost, high energy storage density, high thermal efficiency, and ability to release stored energy at a steady temperature (PCM) [5], [7]. Out of many research performed by researchers based on an application-specific discussion of the thermal characteristics of organic PCMS, inorganic PCMs, and eutectic PCMs [1], [3], [7], [8]. Inorganic PCMs have 0.3-1 W/m K thermal conductivity and possess high latent heat with a temperature range. Additionally, organic PCMs have noteworthy drawbacks, such as high supercooling and corrosive nature. And O-PCMs (organic phase change materials) have been viewed as the best option for TES because of their low vapour pressure, high energy storage capacity, chemical stability, self-nucleating behaviour and commercially available [9], [10].

Organic PCMs are the fossil fuel derivative, showing price dissimilarities and having geopolitical significance. Because of these aspects, need to transfer motivation from commercial organic PCMs to auxiliary bio-based PCM (BPCM) [11]. O-PCMs are ideal for TES due to their low vapour pressure, large energy storage capacity, chemical stability, self-nucleating tendency, and commercial availability. On the other hand, organic PCMs are the fossil fuel derivative, showing price dissimilarities and having geopolitical significance. Because of these aspects, an urgent need to shift the motivation from commercial organic PCMs to (BPCMs). As a promising material for TES, BPCMs composites have concerned with energy storage because BPCMs have some unique properties such as less pollutant, high energy storage, Highly stable, small volume change, and eco-friendly [12]–[15]. But, BPCMs have some basic difficulties, such as low thermal conductivity and leakage during the phase transition stage. To reduce leakage problem and thermal conductivity of BPCMs, a porous material is integrated with BPCMs as support materials, and nanoparticles are integrated with BPCMs to reduce the low thermal conductivity problem of BPCMs [16], [17]. Graphite foam [18], [19], carbon nanotubes (CNTs) [20], [21] metal-organic frameworks (MOFs) [22], [23], mesoporous silica [18], [19], porous hierarchical porous polymer (HPP) [24], [25], coordination polymer-PCP [26], and hierarchical porous carbon-HPC [27], [28] are the types of porous materials that are typically utilized.

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Recently, researchers paid more attention to sustainable bio-based materials, and some biobased porous materials are used to occupy organic PCMs to prepare bio-based PCM composites [29]–[31]. The BPCM composites prepared by porous support carriers mostly have outstanding thermal stability. Nano additives are also used with the BPCMs to enhance the thermal conductivity of BPCMs. Liu et al. [32] synthesized a novel bio-based PCM composite containing PEG as a base PCM and biodegradable castor oil as a support material to fabricate a BPCM composite. They analyzed the thermal stability of the BPCM composites was increased. Jose et al. [33] examined thermo-physical properties of an eco-friendly PCM composite containing isopropyl palmitate as a bio PCM and graphene nanoplate (GnP) as a nano additive. The result shows supercooling of a composite was reduced, and latent heat was enhanced compared with pure PCM. Song et al. [34] experimentally analyzed the thermal stability of the bio-based PCM composite consists porous carbon as a raw material. Porous carbon has a 3-D structure and possesses a high specific area. Results show that the bio-based PCM composite attained outstanding thermal stability. Liu et al. [35] fabricated the bio-based waste fly ash/Capric acid (CA)/CNT composite. And found thermal conductivity of BPCM composites was increased than pure CA. Zhang et al. [36] analyzed a bio-based PCM composite's thermal properties, consisting of silver nanoparticles with modified eggplant-based porous carbon. The result shows thermal conductivity of a BPCM composite is enhanced suggestively and thermally stable with a high loading rate. Zhao et al. [37] was the first researcher to find porous biomass carbon (PBC) by using carbonizing radishes and potatoes by consuming polyethylene glycol (PEG). Experimentally, Zhao et al. Zhao et al. [38] tested the thermal performance of a micro-encapsulated BPCM composite with a PEG/O-Dt core and a WF/HDPE shell. M-BPCM composites demonstrated greater heat conductivity than base PEG. Liang et al. [39] fabricated a Bio-based PCM composite using fatty acid (FA) as a base PCM and wood floor as a support material. The result shows that the FA/WF BPCM composite's thermal stability increased compared to the pure FA.

Several review articles on bio-based PCM discuss thermal properties, porous support materials and nano additive dispersion for improved thermal conductivity, stability, and thermal efficiency based on the bio-based PCMs and different nano additives separately. But they do not focus on the valid reasons and fabrication techniques of the BPCM composites in the single manuscript. Hence, a systematic review to understand the thermal behaviour of BPCMs with synthesis techniques is missing. This work aims to deliver a comprehensive, timely, and in-depth understanding of the most recent successes in research and development of BPCM composites preparation techniques and thermal properties enhancement with valid reasons. In addition, the thermal characteristics of the BPCMs receive a great deal of focus and consideration. The authors provide comprehensive information on (a) the classification and properties of BPCMs, (b) the synthesis technique of BPCMs, and (c) discussing the advancement of bio-based PCMs with an increase in thermal properties with the dispersion of nanoparticles. The article consists of five sections. Section one, Introduction, provides vital information based on bio-based PCM composites and the objective of a present review paper. Section two, TES, offers comprehensive information for the researchers. Section three on Classification of PCMs, discusses types of PCMs with significant properties. Section four, Bio-based PCMs, is detailed information on the bio-based PCMs in this section. Section five, Thermal properties of BPCM composites, thermal conductivity, melting point, latent heat increment or decrement, is discussed in this section with valid reasons. Finally, section six is the conclusion.

2.0 THERMAL ENERGY STORAGE TECHNOLOGY

Effective enhancement in energy efficiency provides a cost-effective technique to decrease pollution and greenhouse gas emissions and promote the use of eco-friendly energy for various applications. Nowadays, thermal energy conservation in solar applications and buildings is crucial. Therefore, TES reduces costs and improves energy efficiency for sustaining calm conditions. Phase change materials store thermal energy in two forms, (a) latent heat and (b) sensible heat, as shown in Figure 1. TES stored by the PCM consists of three steps. Step-1 and step-3 store thermal energy at a variable temperature known as sensible heat (TES); when heat is provided to a PCM, the main equation for sensible heat thermal energy storage and determination of SHTES capacity is shown in Eq. (1) [40]. Step-2 absorbed thermal energy at a constant temperature known as latent heat (TES) by providing heat to a PCM; a main equation for latent thermal heat energy storage is Eq. (2) [40]. LHTES is the relevant and emerging method to support the accessibility and effectiveness of conventional energy. LHTES tends to store 10-14 times more energy than SHTES. Recently, LHTES has had enthusiastic attention due to its high TES density, small temperature variation, and small variation in volume during the phase transition stage [42].

$$Q_{SH} = \int_{T_1}^{T_2} mc_p \, \mathrm{d}T \tag{1}$$

$$Q_{LH} = \int_{T_s}^{T_m} mc_{p,s-m} \, \mathrm{d}T + m\alpha\Delta h + \int_{T_m}^{T_1} mc_{p,m-l} \, \mathrm{d}T \tag{2}$$

In Eq. (1), *m* represents storage mass, *Cp* represents a specific heat of SHS materials under constant pressure, and T_1 and T_2 represent low and high temperatures at which the SHS is maintained, respectively. It is generally accepted that *Cp* is temperature independent so long as it is used in SHS applications within a certain temperature range. In the second equation, where Tm is the melting point of a PCM, $c_{p,s-m}$ and $c_{p,m-l}$ are considered as specific heats of the PCM in its solid and liquid states, respectively, and Δh is the phase change enthalpy.

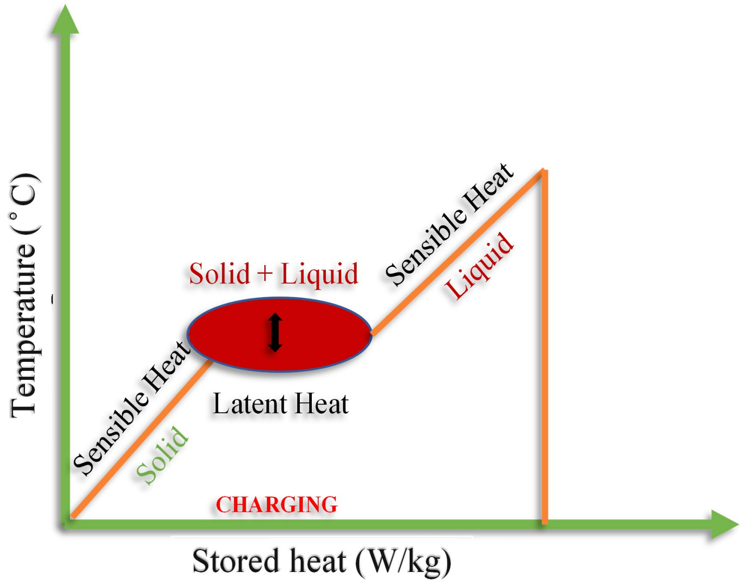


Figure 1. Thermal energy storage process, reprinted with permission from ref [43]

3.0 CLASSIFICATION OF PHASE CHANGE MATERIALS

PCM is a material that can store thermal energy and release it at a consistent temperature while maintaining a high heat of fusion [44]; after being subjected to repeated heating and cooling cycles, the chemical and physical characteristics of PCMs do not change. The temperatures of PCMs can range from -5 to 190° C [45]. Based on their chemical makeup, polycyclic aromatic hydrocarbons (PCMs) are often divided into one of three categories: (a) organic PCMs; (b) inorganic PCMs; and (c) eutectic PCMs [46], as represented in Figure 2. Ideal properties of the PCMs based on thermal performance, design and optimization are:

i. High melting point temperature [47].
ii. High heat transfer capacity and enough heat fusion are produced.
iii. Thermally stable with a low supercooling rate.
iv. Decent economic possibility [46], [48].
v. Self-nucleating properties with no segregation.

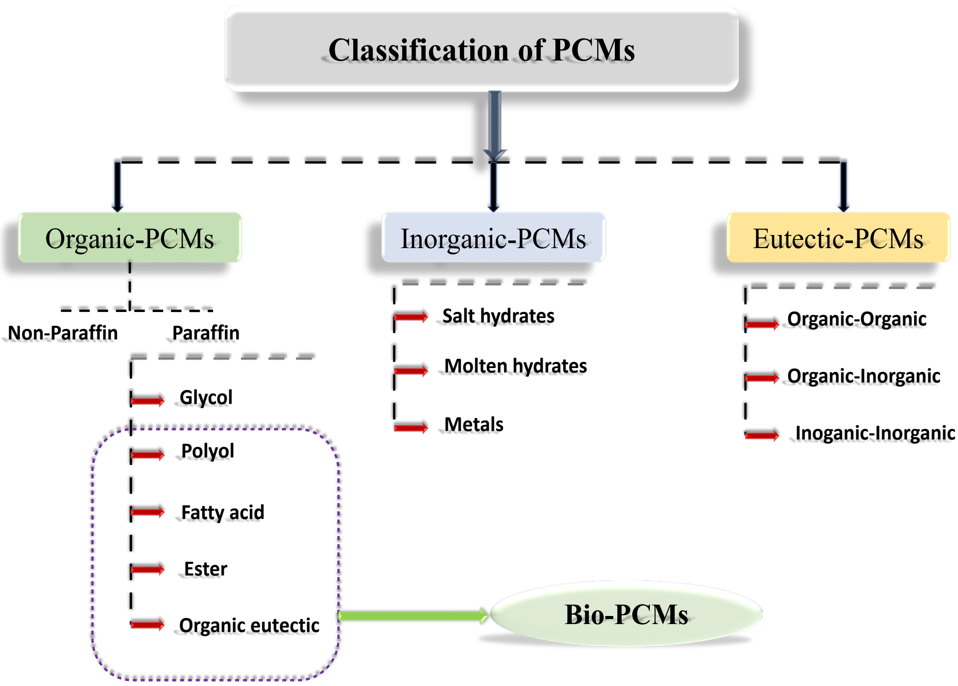


Figure 2. Classification of phase change materials

In this study, we focus on environmentally friendly BPCMs such as polyols, esters, fatty acids, and eutectic BPCMs that directly result from waste vegetable oils, waste products, wood grain, and animal fats.

4.0 BIO-BASED PHASE CHANGE MATERIALS

Bio-based phase change materials (BPCMs) are distinct from other types of phase change materials because they can store or release thermal energy during the transition from the solid to the gel or stable to the concrete phase. According to the literature, BPCMs have energy storage and release rates from -75°C to 175°C with low pollution impact on the environment and reduced carbon footprint. In addition, BPCMs are thermo-physically stable with non-corrosive nature, making them preferable eco-friendly. BPCMs are eco-friendly and biodegradable materials for TES to reduce carbon footprints. So, BPCMs are classified as natural-based PCMs, polyols, commercial, eutectic, fatty acids, organic eutectic and the byproduct of natural substances that are sustainable and kind to the environment, such as palm kernel oil, coconut oil, and other tropical oils, as well as animal fat shown in Figure 3 [49], [50], [2], [51], [52].

4.1 Classifications of Bio-Based Phase Change Materials

Naturally occurring BPCMs are derived using bee wax, coconut oil, and palm oil soya oil. Poly-ethers are derived from PEG-400, 600, 1000, 2000, 6000 and 10000, and fatty acids consist of octa-decanol, lauric acid and cetyl alcohol. Pure temperature PCMs and rubitherm (RT-27, RT-45 AND RT-50) are commercial PCMs. A eutectic bio-based mixture includes palmitic and steric acid, malic acid, capric acid, lauric acid, palmitic acid, and polyols derived from adonitol, sorbitol and erythritol.

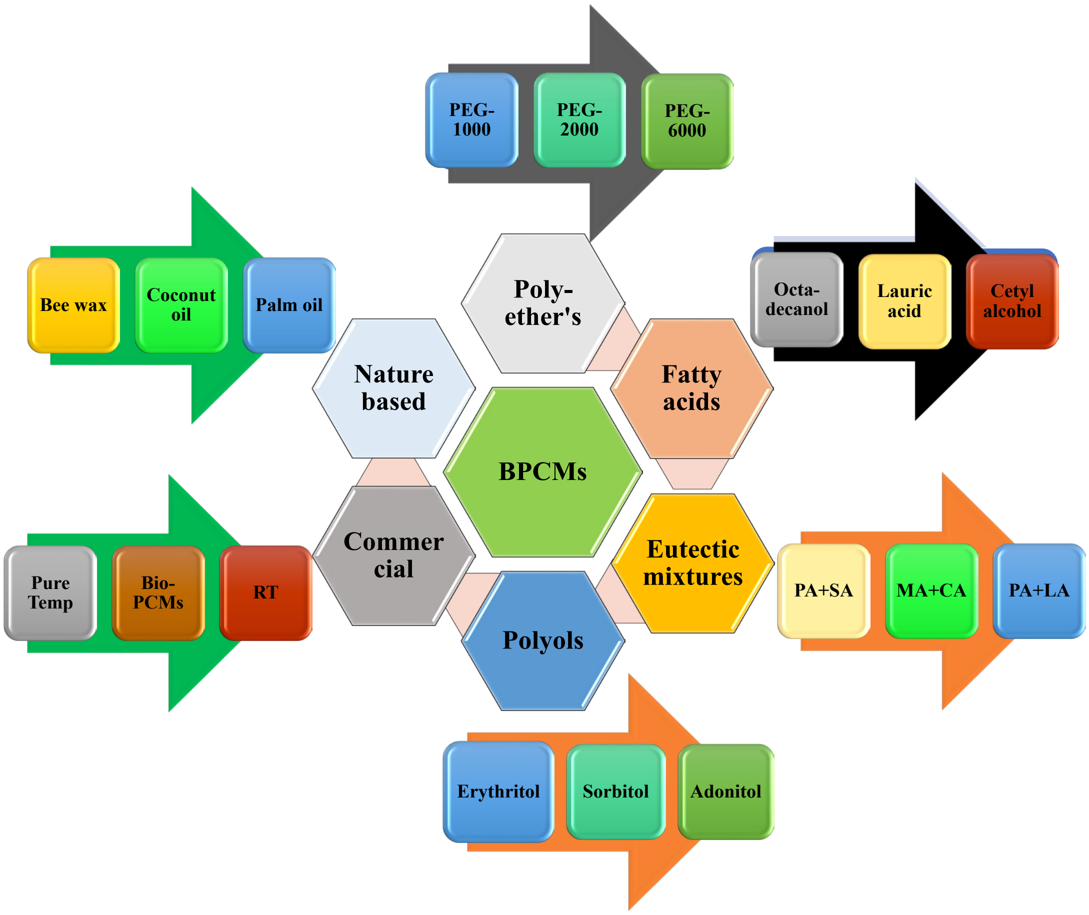


Figure 3. Classification of BPCMs

4.2 Properties of Bio-Based Phase Change Materials for TES

BPCMs are the most investigated and probably used BPCMs for TES applications with low carbon release [53], [54]. BPCMs possess a renewable, less explosive, and eco-friendly, low vapour pressure, a chemically stable inflammable, non-explosive, broad range of melting temperatures, high density and recyclable nature, which allows them for several TES applications [55], [56]. Moreover, the excess availability at a low cost of BPCMs makes them favoured-choice somewhat over conventional PCMs [52], [57]. BPCMs are preferred over the other PCMs due to their significant properties, as shown in Figure 4.

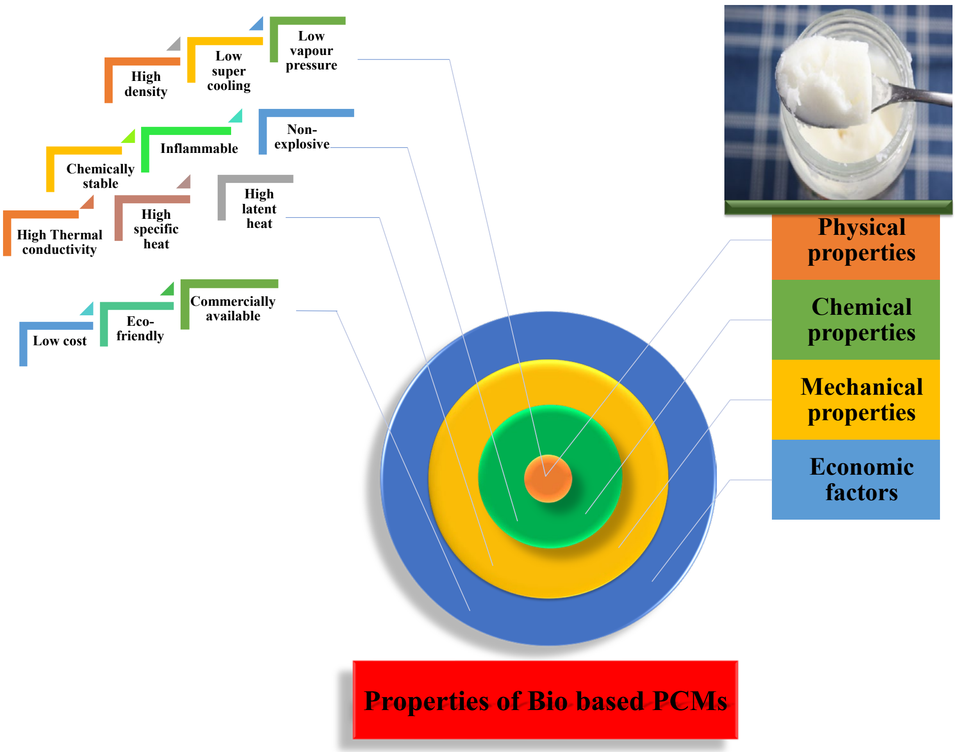


Figure 4. Properties of BPCMs

4.3 In-Corporation Techniques of Bio-Based Phase Change Materials

BPCMs fabrication methods are divided into two types (a) direct incorporation method and (b) indirect incorporation method, as shown in Figure 5. The direct incorporation methods are further classified as immersion, assimilation, recyclable waste and economic framework. It is the easiest way to use waste cooking oils, fatty acids, and bee wax to produce a biodegradable composite with low-cost production. The indirect methods are classified as micro-encapsulation, macro-encapsulation, shape stable and form stable methods. Generally, the micro-encapsulation and macro-encapsulation method is used to reduce the leakage problem of BPCMs because the encapsulation container has good flexibility, large surface area, thermal stability, and strong corrosion resistance.

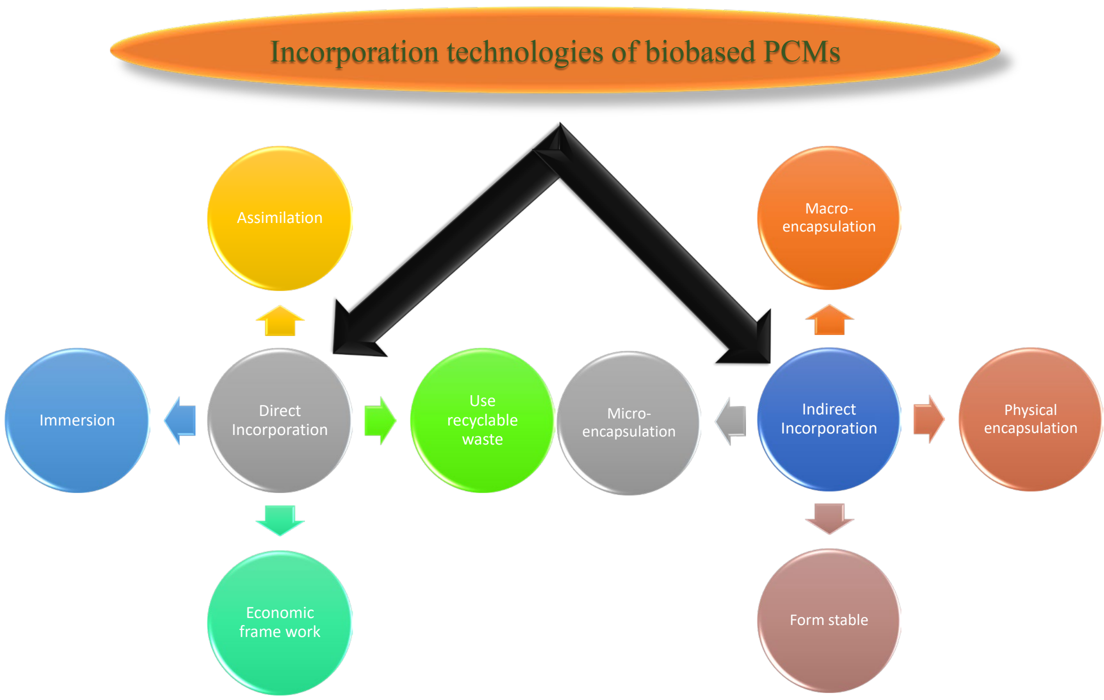
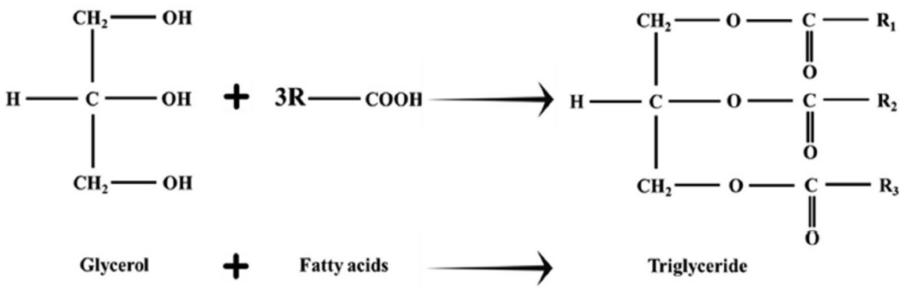


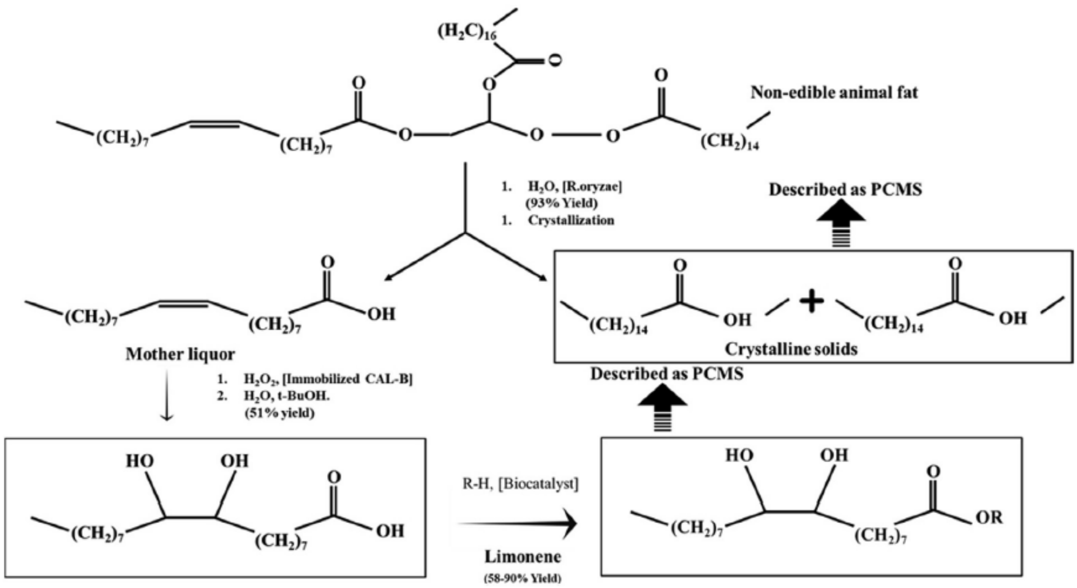
Figure 5. Fabrication methods of BPCMs

Conventional BPCM such as vegetable oil, animal fat and fatty acids have decent properties for TES. Meanwhile, most are bio-degradable and used as bio-degradable PCMs in various applications. Animal fat and vegetable oils are formed by combining three long-chain fatty acids known as tri-esters (triglycerides). Figure 6(a) shows the triester's construction using glycerol and fatty acids, whereas alcohol groups work as nucleophiles. Non-conventional BPCMs produced by animal fat waste and non-edible oils such as chicken feather, lard, and tallow are common waste products generated by agriculture and food industries [58]. Animal fats and non-edible oils tend to be from bio-based PCMs. They are used for TES applications because animal fat waste and non-edible oils contain fatty acids and significant thermal properties. But preliminary studies have been shown in this dimension. A systematic procedure for fabricating BPCM from non-conventional materials (non-edible animal fat) using the biocatalytic reaction is shown in Figure 6(b). Waste of edible oils such as dyeing process [59], burning fuel [60]–[64], biobased plasticizers [65], [66], bio-lubricants [67], polymeric materials [66], [68], detergents, soap [69], cosmetics, bio-origin solvents for pollutants [67], 2nd generation biofuel/gas [70], polyamide for and asphalt binder additive are used for rejuvenating aged-bitumen [71], [72] such as are also showed significant properties for used as BPCMs in TES applications. Figure 6(c) represents the assemblies of WEOs with width and bonding angles of fatty acids.

In general, as was discussed before, there are direct integration techniques (such as immersion and assimilation), indirect incorporation methods (such as macro-encapsulation, micro-encapsulation, physical encapsulation, and form stability), and usage of recycled waste. Encapsulation, surface modification by adding nanoparticles, and physical blending are techniques used to reduce the corrosion problem of BPCMs with the matrix material. Other methods include direct impregnation, direct immersion method vacuum impregnation, macro/microencapsulation, and ultrasonication. The microencapsulation method was the most prevalent approach employed in the BPCM fabrication process. Because the increased cost of production caused by the manufacturing techniques of BPCMs is still insufficient, we still need to locate the best possible materials suited for encapsulating BPCMs.



(a)



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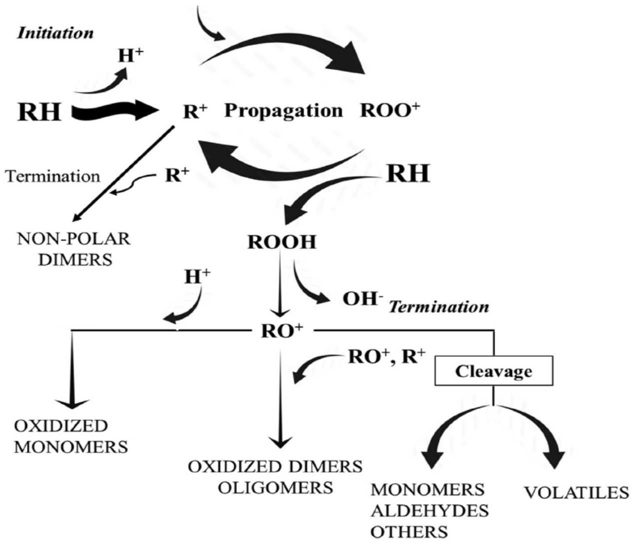


(c)

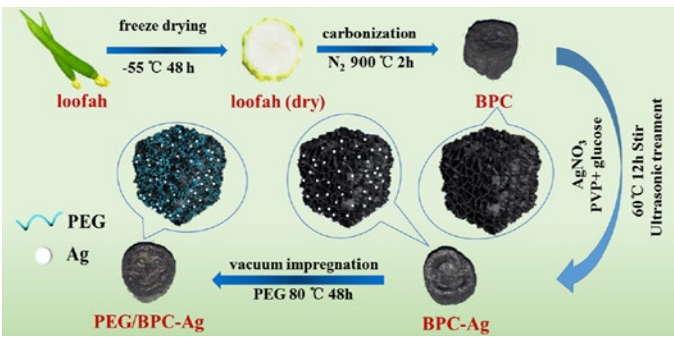
Figure 6. (a) Assembly of tri-esters, (b) Fabrication of BPCM from non-conventional materials (non-edible animal fat) using the biocatalytic reaction, and (c) Assemblies of WEOs with fatty acids [73]

5.0 THERMAL PROPERTIES OF BIO-BASED PHASE CHANGE MATERIALS

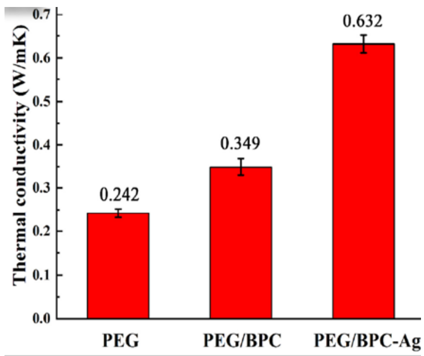
However, difficulties with leakage and poor thermal conductivity are key downsides of BPCMs. Because of these drawbacks, current researchers have been able to undertake an immense number of studies to tackle all of the issues described above [58], [74]. And researchers looked for a workable answer to the problem of the BPCMs' poor thermal conductivity to find a remedy [75]–[78] by adding highly conductive nanoparticles with BPCMs to make an eco-friendly composite [79], [80]. Furthermore, shape stable, the researchers use foam stable, micro-encapsulation and macro-encapsulation methods to reduce leakage problems of BPCMs during phase transition [81].

Boussaba et al. [82] fabricate a novel (BPCM) composite consisting of a novel hydrogenated Palm Kernel fat as a biobased PCM and cellulose fibers as a support material to find the thermal properties of BPCM composite. The direct immersion method was used to prepare a cheap and eco-friendly composite. Results show that the BPCM composite's thermal conductivity was increased as compared with bio PCM by 430 % with the addition of graphite powder. Additionally, the latent heat of BPCM composite was calculated to be 40.27 J/g during melting and 41.13 J/g during solidified processes. Furthermore, the thermal conductivity of a BPCM composite was enhanced because graphite powder has a good interaction with the PCM and forms a stable composite; due to this, the conductive path generated and the heat transfer rate improved.

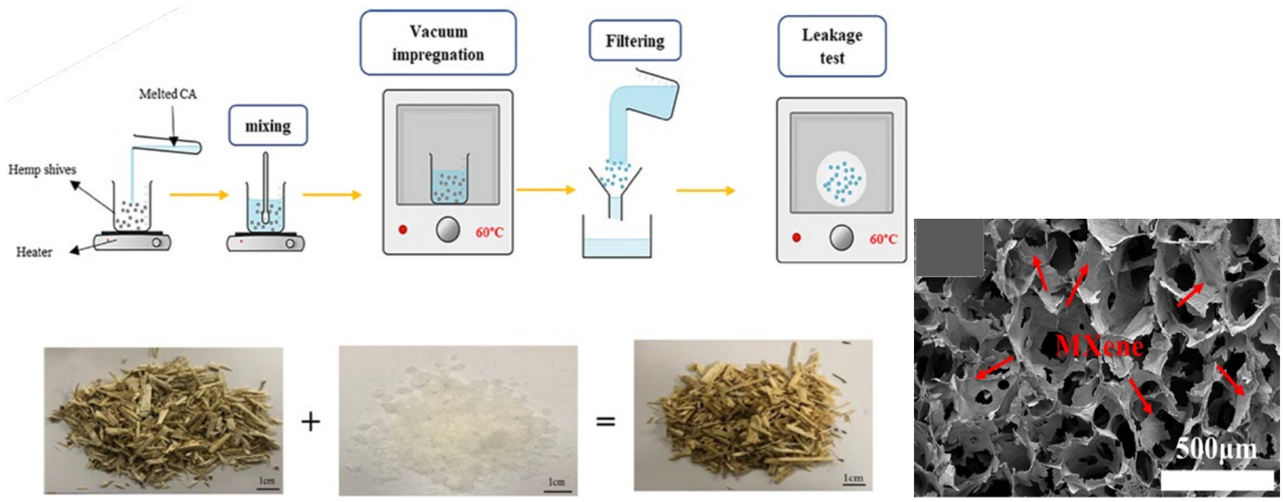
Using loofah-based porous carbon as the support material and PEG as the base PCM with Ag nanoparticles, Xiao et al. [83] conducted experimental investigations into the thermal performance of BPCM. As can be seen in Figure 7(a), the BPCM composite was made using a vacuum impregnation technique. The composite has a higher thermal conductivity than the base PEG by 0.632 W/m K, as shown in Figure 7(b). Moreover, 92.3% efficiency after 100 heat cycles were recorded, and the composite was thermally stable. Sawadogo et al. [84] found hemp shives as PCM and CA supporting material in the BPCM composite's thermal properties.



(a)



(b)



(c) (d)

Figure 7. (a) Vacuum impregnation method to fabricate the PPC-PEG/Ag BPCM composite [83], (b) thermal conductivity of BPC-PEG/Ag composite[83], (c) vacuum impregnation method to fabricate hemp shives/CA BPCM composite [84] and (d) SEM image of Mxene/PEG-PPF bio-based composite [85]

Figure 7(c) shows a vacuum-impregnated BPCM composite. The composite melts at 78.7 J/g and freezes at 76.4 J/g. The composite melted at 28.9 °C and froze at 23 °C. Sheng et al. [85] analyzed the thermal properties of a form-stable composite PCM using new bio-based pomelo peel foam (PPF) as support material and polyethylene glycol (PEG) as a PCM with Mxene. FSCPCMs have better thermal conductivity than PCM base materials (0.25 W/m K). Figure 7(d) shows that ultrasonication and hoover drying equally distribute MXene throughout the PPF.

Coconut oil served as the basic material in the bio-based PCM composite created by Nazari et al. [86], which also included oleic (OA) and linoleic (LA) acids as the PCM. Almost as good as pure PCM, the data showed that the thermal conductivity of the composite was 0.35 W/m K. A composite's latent heat was between 40 and 100 J/g. A composite's thermal stability was also not affected by 700 heat cycles. Parameshwaran et al. [87] synthesized micro-encapsulated bio-based phase change materials (MBBPCMs) using lauric acid (LA) and urea formaldehyde (UF). In-situ polymerization created MBBPCM composites. The composite has 54.32 J/g latent heat and 42.65 °C melting temperature. Jeong et al. [88] created a porous boron nitrite-bio PCM SSBPCM to detect thermal conductivity and reduce leakage. This study's SSBPCM was vacuum impregnated. SSBPCM thermal conductivity was 0.729 W/m K, 450% higher than pure PCM (0.152 W/m K). Boron nitrite's thermal conductivity increased the composites. Jeong et al. [52] used porous exfoliated graphite nanoplatelets as a supporting material and bio PCM (soybean oils, beef fat, and coconut oils) as a base material to evaluate BPCM thermal characteristics. BPCMs were hoover impregnated. BPCM has 375% higher heat conductivity than bio PCM. Exfoliated graphite nanoplatelets enhanced composite thermal conductivity.

Yang et al. [89] synthesized a bio-based PCM composite employing palmitic acid as a base PCM and graphene nanoplatelets (xGnP) as an enhancer to test BPCM thermal characteristics. The BPCM composite's thermal conductivity was 1.08 W/m K at 7.87 wt%, 237.5% higher than pure PCM (0.32 W/K). xGnP's high aspect ratio and specific surface area enhanced composite thermal conductivity. Saeed et al. [90] made a BPCM composite using coconut and palm oils as bases and graphene nanoplatelets (xGnP) as supporting materials to measure thermal conductivity. The thermal conductivity of coconut oil/xGnP was 1.33 W/m K; palm oil/xGnP was 1.26 W/m K, up 414 and 437% from pure coconut and palm oils, respectively. The high aspect ratio and large specific surface area of xGnP [91] enhanced composite heat conductivity. Lu et al. [92] created a bio-based PCM composite by employing polyurethane (PU) as a basis and wood powder (WP) as a supporting element. This combination served as the foundation for the composite. The results indicate that the latent heat of a BPCM composite was 134.2 J/g when it was melting and 132.4 J/g when it was solidifying. In addition to this, they discovered that the composite had a thermal efficiency of 98%. Naresh et al. [93] synthesized an ecologically friendly bio-based PCM composite from hexadecanol. They employed modified porous fly ash to test BPCM composite thermal properties. Vacuum impregnation created the BPCM composite. The BPCM composite had a higher thermal conductivity than pure PCM, which was 0.3397 W/m K. Additionally, composite latent heat was 114.42 J/g, and thermal reliability was assessed up to 1000 cycles.

Based on the authors' concerns, the carbon-based nanoparticles used with BPCMs has a significant drawback; the composite's latent heat is reduced compared to the base PCM. But according to the literature, the bio-based nanoparticles combined with BPCMs have three-dimensional structures. When coupled with bio-based nanoparticles, the bio-based phase change materials (PCMs) produce a consistent solution. Another reason the utilization of BPCMs is more effective than that of the other PCM categories is that the thermal properties of BPCMs are more uniform than those of the other categories of PCMs. BPCMs are suited for use in applications requiring thermal energy storage since their latent heat tends to grow as the concentration of the material drops as they go away from the base.

6.0 CONCLUSIONS

The call for energy in the world is increasing speedily and the significance of using fossil fuels is pollution and greenhouse gas emissions in the environment. So, urgent need to find biodegradable, eco-friendly, and sustainable materials to reduce the carbon footprint problem of domain. There has been a growth in the usage of BPCMs for TES due to the unique qualities that BPCMs possess. These properties include non-toxicity, suitability for latent heat, low explosiveness, high melting point, high thermal stability, zero-supercooling, and self-nucleating reaction. Because they come from natural sources, BPCMs are considered the most natural type of PCMs. As a result of being completely hydrogenated, BPCMs offer exceptional thermal stability for operations involving melting and freezing up to one thousand heat cycles without the slightest possibility of oxidation occurring. BPCMs exhibit zero degrees of supercooling during the freezing process and just a tiny volumetric change and a lower melting point in the low-temperature region.

In addition, BPCMs can store sufficient latent heat and release it when necessary. They are also appropriate for use in macro-encapsulation, micro-encapsulation, and physical-chemical processes. Additionally, BPCMs have disadvantages, such as low thermal conductivity and phase separation problems during phase transition. To reduce phase separation and low thermal conductivity problems, additional research is needed to find the best suitable encapsulation material and nano additives based on biodegradable, eco-friendly, low-cost, highly stable and renewable support for BPCMs. Furthermore, pay more attention to the BPCMs to reduce the use of commercial non-biodegradable PCMs and promote the use of eco-friendly PCMs. PCMs produced by nature are considered for TES purposes. Improvement in the nano-encapsulation method is required to reduce leakage problems and improve the thermal conductivity of the BPCMs.

7.0 SUMMARY

Some highlighted points to adopting bio-based PCMs for TES:

i. Bio-based PCMs are suitable for latent heat, low supercooling, high melting temperature, thermally stable over a different temperature range, non-toxic, less flammability, and self-nucleating abilities.
ii. According to the characteristics of BPCMs are suitable for different TES applications such as chilling and air conditioning, heat recovery systems, heat storage and release, building heating and cooling and solar heat condensation.
iii. The accessibility of bio-based PCMs is more accessible compared to organic and inorganic PCMs. But most researchers used vegetable and animal oils as BPCMs; hence, more research is required to find the alternate BPCMs produced by plants.
iv. Besides the advantages of BPCs, numerous limitations also associated with them are low thermal conductivity, leakage problems during phase change, volume change during phase change and odour generation, which delay their extensive applications. So, we need to do significant research work to overcome these drawbacks.

8.0 ACKNOWLEDGEMENT

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