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Phase Change Materials for Life Science Applications

Mina Zare and Kirsi S. Mikkonen**

Phase change materials (PCMs) are a class of thermo-responsive materials that can be utilized to trigger a phase transition which gives them thermal energy storage capacity. Any material with a high heat of fusion is referred to as a PCM that is able to provide cutting-edge thermal storage. PCMs are commercially used in many applications like textile industry, coating, and cold storage typically for heat control. These intriguing substances have recently been rediscovered and employed in a broad range of life science applications, including biological, human body, biomedical, pharmaceutical, food, and agricultural applications. Benefiting from the changes in physicochemical properties during the phase transition makes PCMs also functional for barcoding, detection, and storage. Paraffin wax and polyethylene glycol are the most commonly studied PCMs due to their low toxicity, biocompatibility, high thermal stability, high latent enthalpy, relatively wide transition temperature range, and ease of chemical modification. Current challenges in employing PCMs for life science applications include biosafety and/or engineering difficulties. The focus of this review article is on the life science applications, evaluation, and safety aspects of PCMs. Herein, the advances and the potential of employing PCMs as a versatile platform for various types of life science applications are highlighted.

1. Introduction

The increased need for energy and depletion of fossil fuel resources have wreaked havoc on the environment. Concerns regarding environmental preservation and protection drive researchers to seek new renewable energy sources (RES) and develop renewable power system technologies. Energy storage systems can be classified by their response time, storage duration, function, and the most common technique is to categorize them by the type of energy they store (electrical, chemical, mechanical, thermochemical, thermal).[1] Thermal energy storage (TES) is a well-recognized approach that possesses the capability to address energy redistribution requirements. Besides, TES is able to contribute to the reduction of greenhouse gases being emitted into the ecosystem. TES techniques assist to bridge the gap between available energy sources and demand, allowing RES to be used more effectively as needed.[2,3] There is an increasing drive to enhance TES efficiency and, reduce their prices.[3]

The different types of TES systems include latent heat storage (LHS) that employs latent heat of phase change materials (PCMs) and is classified into [organics (paraffin and non-paraffin like fatty acids (FAs), alcohols, and esters), inorganic (metal alloys, and salt hydrides:, e.g., $MgCl_2$, KCl, carbonate salts), and eutectics (which are mixtures of inorganics and/or organics)], sensible heat storage (SHS) involves storing heat by raising the temperature of storage material that is in a solid, liquid, gaseous, or supercritical state (e.g., corkboard, dry and wet earth/soil, wood, thermal oil, rocks, water (H_2O), concrete, molten salt, stones, bricks, plasterboard, and), and thermochemical heat storage (TCHS) which exploits the reversible chemical reaction via thermochemical materials (TCMs) and is further categorized into liquid absorption materials, physical adsorption materials (silica gel and zeolite), and chemical reactions through composite materials or solid chemical reaction materials (**Figure 1**a).[2,4–7]

PCMs offer an appropriate mode to store thermal energy as latent heat thermal energy storage (LHTES) because of their high thermal storage density in almost isothermal conditions.[4,5,8] Melting point and solidification temperature, thermal conductivity, latent heat, and storage density are important thermophysical parameters that are used for the selection of PCMs. Each PCM has its own set of advantages and disadvantages, limiting its usage to specific applications.[4] The effectiveness of each PCM's thermal storage is determined by melting point, while the heat capacity of the TES system is determined by the PCM latent and sensible heat.[9] The cooling power or thermal conductivity governs the charge and discharge rate of thermal energy.[10] A summary of the desirable features of PCMs is illustrated in Figure 1b.[5,11,12] To achieve these properties, TES systems must be designed to have a low rate of energy deterioration and fewer inherent irreversibilities. It is acceptable to conclude that TES systems that have undergone exergy analysis may be optimized for operational performance, particularly during the charging/discharging process. Acar Canan (2018)

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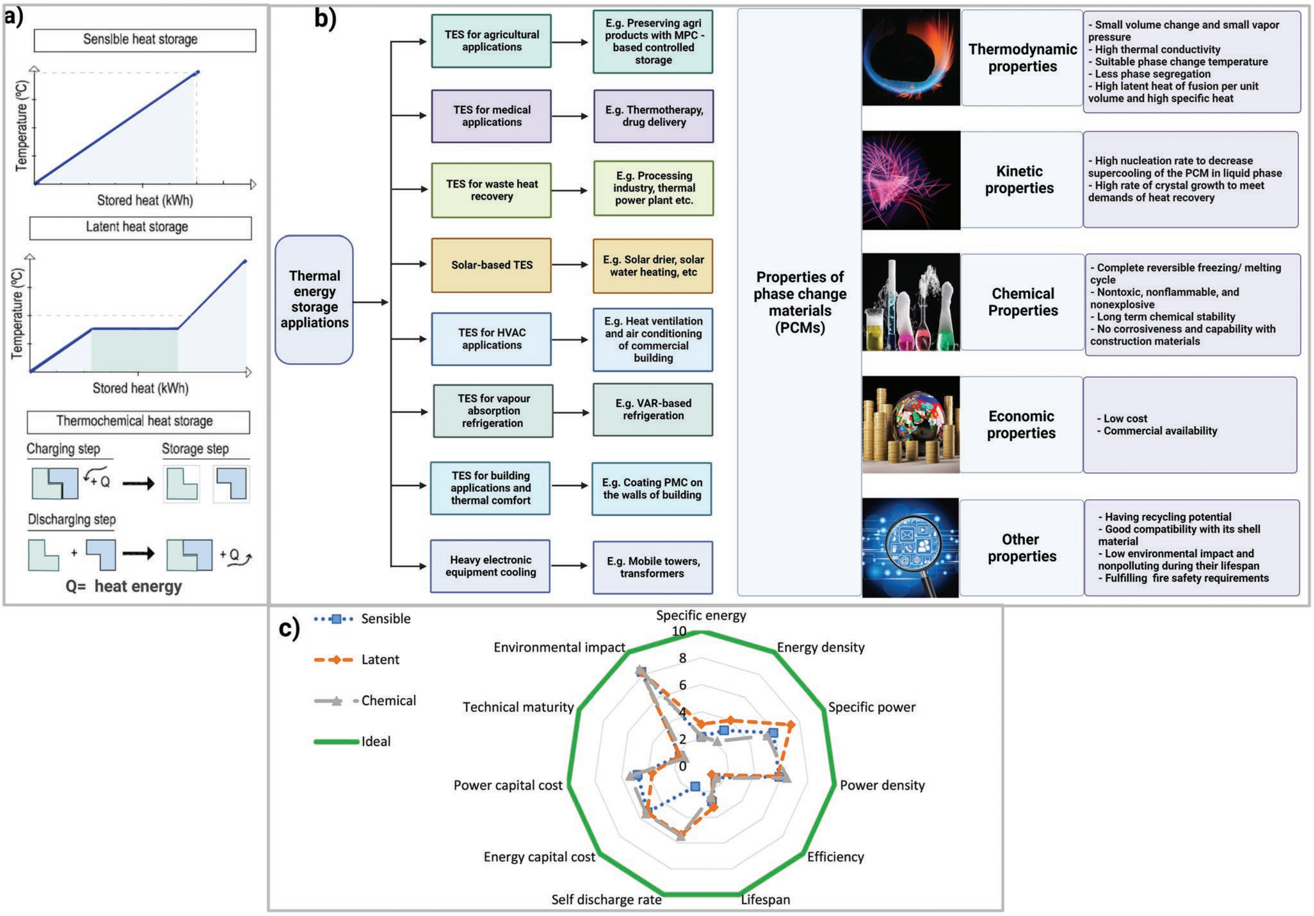

Figure 1. a) Illustrates the thermal energy storage techniques (TES; latent, sensible, and thermochemical storage), b) Represents the important properties of PCMs that make them suitable for life science applications, and c) Depicts the technical, economic, energetic, and environmental comparison of selected TES systems. Latent (4.43/10), chemical (3.89/10), and sensible (3.89/10) are the average normalized rankings of TES systems from highest to lowest. (c) Reproduced with permission.[13] Copyright 2018, Wiley-VCH GmbH.

reported the comparison results in the range of 0–10 based on the equations. The ideal case demonstrates the highest possible level of efficiency, and lifespan, specific power and energy, energy and power density, technical maturity, and the lowest possible power and energy capital cost, self-discharge rate, and environmental impact.[13] Figure 1c represents the PCMs' characteristics.

In a previous review, Sadeghi (2022), discussed the thermal energy management of batteries and high-heat-flux electronic devices, and the capability of the TES systems.[2] Costa and Kenisarin (2022) produced a database of metallic PCM's thermophysical features and potential impact in diverse fields, for instance, bioengineering, electronics, solar energy storage, cooling and heating, and beyond.[8] Chavan (2022) covered the recent progress in TES and its usages such as waste heat recovery, solar-based TES, building applications, thermal comfort, heavy electronic equipment cooling, vapor absorption refrigeration (VAR), and Heating, ventilating, and air-conditioning (HVAC) applications.[14] An increasing number of recent research addresses the use of PMCs in human body, detection or sensing, biological, barcoding, drug delivery, and medical applications. However, there is no review comprehensively discussing the life science applications of TES and PMCs materials. Based on our literature survey we concluded that a review of the life science applications of PCMs is a required reference. Besides, the evaluation and safety aspects of TES will be explored in this review. Furthermore, the challenges and recommendations of PCM applications will be addressed in order to assist energy technologists and streamline future research.

2. Phase Change Materials (PCMs)

LHS is divided into four categories based on their manner of phase transition: gas-liquid, solid-gas, solid-liquid, and solid-solid. PCMs are a category of advanced materials that are used to store thermal energy as latent heat (**Figure 2**). They play an essential role in the effective use and conservation of waste heat and TES.[15] PCM is a nebulous term used to describe a material that has a high latent heat of fusion when it comes to melting or solidifying at a practically constant temperature.[16] They have developed a new class of thermo-responsive materials for controlled release, in which payloads enclosed in a solid matrix are only released when the PCM is melted to cause a solid-liquid

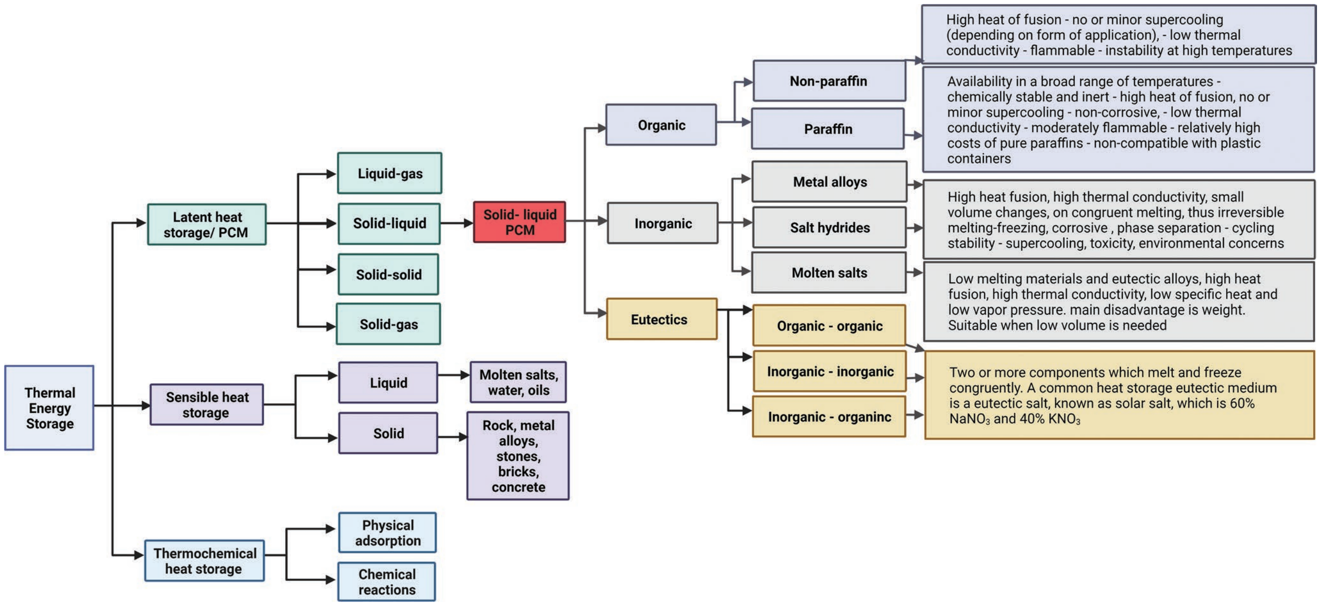

Figure 2. Displays thermal energy storage (TES) system classification and the PCMs subcategories.

phase shift. PCMs can store and release a considerable quantity of heat during phase transition over a very small range of temperature fluctuation. For instance, a comparable volume of PCM can store or release 5–14 times more heat than traditional thermal storage materials like H_2O or rocks. PCMs have been extensively investigated for use as thermal materials in heat control.[17] It should be noted that the storage or release of energy in PCMs during phase transition is merely one reflection of changes in intermolecular interactions (e.g., Van der Waals forces and hydrogen bonding). Other physicochemical properties for instance density and mobility are also affected by changes in intermolecular interactions. PCMs have also been investigated as functional materials for different purposes, taking advantage of the changes in physicochemical characteristics that occur during the phase transition, for example, information storage, detection, and barcoding.[17] The features needed for a material to be employed as a PCM are tabulated in **Table 1**.

2.1. Organic

Paraffin waxes or alkanes with saturated, aliphatic hydrocarbons, and the chemical formula C_nH_{2n+2}, where $20 \leq n \leq 40$, are commonly referred to as paraffin. The long and straight-chain releases a lot of latent heat during crystallization, and the melting temperature rises as the chain lengthens with the number of carbon atoms.[18] Paraffin is a good thermal storage material as a result of this, as well as its availability over a wide range of temperatures. However, because of the high price of pure paraffin waxes, technical-grade paraffin is commonly utilized.[16] Technical-grade paraffin is made up of a variety of hydrocarbons with varying chain lengths, and as a result, they have a higher phase transition temperature than pure paraffin. Besides, their high fusion temperatures, paraffin waxes are chemically stable and inert, making them dependable and predictable. Despite these benefits, paraffin waxes have many drawbacks that limit their usage, including limited heat conductivity, incompatibility with plastic containers, the high price of pure paraffin, and mild flammability.[18,19] Guo et al., (2022), designed the microsphere-structured phase change composite using paraffin, and graphene oxide aqueous solution to prepare a stable Pickering emulsion without using additives or emulsifiers. They achieved a high thermal conductivity, maintaining high latent heat of phase transition and preventing leakage of PCMs. They revealed that the addition of polydopamine enhances the absorption of sunlight and exhibits excellent photothermal properties (sensing light irradiation, apparent temperature enhancement, and rapid heating rate). This is an efficient and scalable technique that provides new insight into multi-functional PCMs, thermal energy harvesting devices, and intelligent sensing and smart application of PCMs.[20]

Non-paraffin, organic PCMs, are esters, fatty alcohols, glycols, and FAs, for instance, 1-tetradecanol lauric acid, acetic acid, 1-dodecanol capric acid, 9-heptadecanone, oleic acid, acetamide, and phenylacetic acid. These materials have different properties, however, they all have a few common qualities, some advantageous and others unfavorable, such as huge fusion temps and no or restricted supercooling for FAs, and instability at high temperatures, low thermal conductivity, and inflammability.[16,21] Unlike paraffins, these "green" PCMs are "food-grade", meaning they are safe to eat. Bio-based PCMs have found success in food industries and cosmetics due to their low toxicity and biocompatibility. They have recently shown promise in architecture and construction and biological applications including smart medicine delivery systems and green solvent formulations.[22–24]

Polyethylene glycol (PEG) is a typical organic and a versatile PCM with good biocompatibility, non-toxic and non-corrosive nature, high thermal stability, high latent enthalpy, relatively wide transition temperature range, and ease of chemical modification.[25] PEG decreases intermolecular forces among

Table 1. Features needed for a material to be employed as PCMs.[5]

Thermal	Physical	Chemical	Kinetic	Others
High specific heat value	–	Compatible with container material	Good nucleating features	–
High thermal conductivity	High density	Non-toxic; non-flammable	No phase segregation	–
High latent heat capacity value	Small phase transition volume change	Non-corrosive	No sub-cooling	Easily available
Melting point in the desired operating temperature range	Small vapor pressure	Chemically stable over a number of freeze-thaw cycles	No super-cooling	Low cost

polymer chains, increases extensibility and flexibility, and inhibits undulations or cracks in a polymeric film, therefore is commonly used as a plasticizer in packaging materials.[26] Additionally, it is employed as a solubilizer, solvent, surfactant, capsule, or suppository lubricant for pharmaceutical excipients.[27,28] The heat capacity and thermal conductivity of PEG PCMs for TES applications have been studied. The phase transition temperature and enthalpy, thermal conductivity, and thermal stability were measured. The heat capacity of PEG was analyzed using a combination of differential scanning calorimetry (DSC) and physical property measurement systems. The heat capacity curve fitting was used to calculate the thermodynamic functions.[29] Yazdani et al., (2021), reported PEG-cellulose nanofibrils with form control and solid-liquid transition for TES. They fabricated PEG-cellulose nanofibril hydrogels and processed them into 1D, 2D, and 3D structures through wet spinning, solution casting/molding, and additive manufacturing (direct ink writing). The DSC result represents that phase change nanofibers have remarkable repeatability in LHS after 100 heating/cooling cycles. Additionally, their outcomes have revealed that the light-to-heat conversion and thermal regulation of phase change fibers, outperform those of reference, commercial insulation materials.[30] Abdalkarim et al., 2019, functionalized a series of ultrafine PEG/poly (3-hydroxybutyrate-co-3-hydroxy valerate)/cellulose nanocrystal-zinc oxide phase change composite nanofibers via the electrospinning process. They obtained nanocomposites with photo-TES potency that could be employed as thermally regulated in vitro drug release. Thermal treatment of phase change nanofiber composites for a short period did not alter their chemical structure.[31]

2.2. Inorganic

Inorganic PCMs have similar melting enthalpies per mass as organic PCMs, but because of their high densities, they possess greater enthalpies per volume. They have a strong thermal conductivity and a wide temperature range, as well as acute melting points. Salt hydrates and metals are two groups of inorganic PCMs investigated for life science applications.

Metals, small specific heats, large heats of fusion per unit volume, small heats of fusion per unit weight, relatively low vapor pressures, and high thermal conductivity are all characteristics of these materials.[16,21] Due to their large densities and relatively high melting temperatures, these materials were previously ruled out as PCMs. However, recently metal PCMs, have become much more practical due to advances in nanomaterial production technology.[32,33] The metal PCM's high thermal conductivity and crisp, well-defined melting behavior make them appealing for a variety of uses, particularly as absorptive heat sinks in electronic components.[16,34] Furthermore, the wealth of metallurgical knowledge developed over the previous century makes it simple to create their alloys with regulated temperatures of melting and latent heat. Metals having low melting temperatures (cadmium, Cd; tin, Sn; indium, In; lead, Pb; bismuth, Bi, and their alloys) are particularly interesting.[16]

Salt hydrates are salts of inorganic materials that contain *n* moles of H_2O molecules and form a crystalline structure with the generic formula AB*n* H_2O. Hydrogen bonds or ion-dipole are the most common types of bonding. The H_2O molecules are well-defined in their location and orientation inside the structure, while H_2O is more tightly aligned to the anion in certain configurations and to the cation in others.[35] Salt hydrates are formed by dehydrating and hydrating a salt, a process that is akin to freezing and melting in thermodynamics. A hydrated crystal breaks up at the melting point into a lower hydrate with *m* moles of H_2O or anhydrous salt and H_2O.[36–38]

Currently, salt hydrates are the most well-known type of PCMs and have undergone substantial research, particularly for their usage in TES systems based on latent heat. Comparatively high thermal conductivity (twofold of pure paraffin wax), high latent temperatures of fusion per unit volume, and minor volume changes upon melting are among the most appealing qualities of salt hydrates. They are also non-corrosive, compatible with polymers, and lower in toxicity. $CaCl_2.6H_2O$ and $Na_2SO_4.10H_2O$ are the most widely accessible salt hydrates.[39]

The incongruent melting of salt hydrates is a big issue. The solution becomes supersaturated near the melting temperature because *n* or *nm* moles of hydration H_2O are insufficient to lower hydrate or dissolve anhydrous salts. The anhydrous or lower hydrate salt sits in the bottom of the container due to its comparatively large densities, making it unavailable for recombination with H_2O during the reverse process of freezing. Mechanical stirring, PCM encapsulation, using extra H_2O to prevent supersaturation, or changing the chemical can all help to solve this problem.[16]

Other issues of salt hydrates are difficulty in crystal nucleation, which causes the liquid to become supercool and corrosiveness. This results in energy loss and freezing at lower temperatures.[40] This is a critical flaw as it alters the temperature of the phase change.[41]

2.3. Eutectics

Eutectics are minimal boiling mixes of more than two chemicals that melt and freeze in the same way. The sharp phase change temperature is one of their advantages. Numerous FA eutectics have been produced and shown to possess appealing qualities. They freeze and melt congruently without segregation. The majority of the eutectics for air cooling applications examined in the literature are organic in origin. However, some of them have an unpleasant odor that limits their usage. There is limited literature on their thermophysical characteristics, due to their property determination, synthesis, and analysis being expensive and time-intensive. The component materials, whether organic or inorganic, determine their toxicity.[5,42]

2.3.1. Eutectics Mixture of FAs

While green FAs are a viable alternative for controlled release due to their high biocompatibility, obtaining a PCM formed of a pure FA with a melting temperature near the human body temperature (37 °C) is problematic. Furthermore, during solidification, a single FA tends to develop a highly crystal solid structure, decreasing the drug's encapsulation capacity, generating unwanted burst release, and pushing the payloads to be phase-separated from the FA matrix.[43,44]

To cope with these issues, a eutectic mixture of two or more FAs with melting points lower than all constituents has been proposed as a replacement for single-component FAs to obtain desirable melting points while modifying the FAs' crystal growth behavior to boost drug loading capacity.[45,46] In one case, a 4:1 weight ratio of lauric acid (44 °C melting point) and stearic acid (69 °C melting point) produces a eutectic mixture with a single solid-liquid phase transition at 39 °C.[45] Significantly, the phase shift of such a eutectic mixture may be triggered more readily under heating than either lauric acid or stearic acid.[16]

Table 2 summarizes the pros and cons of PCMs.

Table 2. Pros and cons of different types of PCMs.

PCM Type	Advantages	Disadvantages
Organic, for example, paraffin wax, fatty acids (FAs), vegetable oils	Non-corrosive, eco-friendly A broad range of temperatures is available No phase segregation Good compatibility with a broad range of containers because of non-reactive nature Stable over many freeze-thaw cycles No sub-cooling and super-cooling Chemically, physically and thermally stable	Varying levels of toxicity Low flash point, flammable Low phase change enthalpy Costly in pure form Non-compatible with plastic containers No sharp phase transitions Instability at higher temperatures Poor thermal conductivity values Except for some FAs, large volume changes occur during phase transition.
Inorganic, for example, salt hydrates	Low vapor pressure Sharp melting temperature causes a sharp phase transition Low cost High thermal energy storage capacity Easily available Good thermal conductivity	Incompatible with metallic containers Phase segregation Show super-cooling and sub-cooling
Eutectic	Sharp melting and boiling points Organic phase change material has a lower volumetric storage density	Costly

3. Evaluation of TES of PCMs

Principally, there is a distinction to be made between Analysis (which includes measuring technique (or procedure), assessment, and interpretation) and Method. Regrettably, even under official standards, this is inconsistently implemented (e.g., Thermogravimetric analysis (TGA) vs TG).[47] The thermal analysis (TA) techniques may be classified based on three types of physical factors to be evaluated (heat flux or temperature, mass, mechanical, and other characteristics). **Table 3** represents the TA techniques, methods, abbreviations, and their output properties. This section summarized the most prevalent methods for determining the characteristics of PCMs.

Wang et al., (2021), designed a temperature and pH dual-stimuli-responsive phase-change microcapsule using silica-microencapsulated *n*-eicosane (PCM) with a poly (NIPAM-co-AA) layer for smart drug delivery. They have used differential scanning calorimetry/TA DSC/TA instruments to determine the phase-change behaviors of samples, and evaluate the energy storage efficiency (E_{es}) (Equation (1)), and energy storage capability (C_{es}) (Equation (2)) using the following equations.[53]

$$E_{\mathrm{es}}\,(\%)=\frac{\Delta H_{\mathrm{m,sample}}+\Delta H_{\mathrm{c,sample}}}{\Delta H_{\mathrm{m,PCM}}+\Delta H_{\mathrm{m,PCM}}}\times 100\% \tag{1}$$

$$C_{\mathrm{es}}=\frac{\left(\Delta H_{\mathrm{m,sample}}+\Delta H_{\mathrm{c,sample}}\right)\cdot\Delta H_{\mathrm{m,PCM}}}{\left(\Delta H_{\mathrm{m,PCM}}+\Delta H_{\mathrm{m,PCM}}\right)\cdot\Delta H_{\mathrm{m,PCM}}}\times 100\% \tag{2}$$

Where ΔH_{m} and ΔH_{C} are the melting and crystallization enthalpies for the sample and PCM.

Additionally, the thermal stability was characterized with a thermogravimetric analyzer (TGA, TA instrument) under a nitrogen atmosphere at a heating rate of 10 °C. The thermal conductivity was evaluated by a thermal conductivity tester by means of the transient plane source method. Finally, the thermal regulation behavior was analyzed using an infrared thermal imaging camera.[53] Yang et al., (2021), studied melamine foam-based flexible PCMs to enhance the photothermal conversion and shape memory properties for energy storage applications. The heat transfer capacity was investigated with 3D infrared thermography. Furthermore, the thermal conductivity, thermal gravimetric, and melting/crystallization behavior of PCM-based foam were evaluated using a thermal conductivity meter, TGA, and DSC, respectively.[54] Song et al., (2021), developed a carbon aerogel based-composite PCM derived from kapok fiber, by incorporating $\mathrm{Fe_3O_4}$ nanoparticles and encapsulating lauric acid with ultra-high latent heat. The magnetic property was evaluated with a magnetometer at room temperature. Moreover, the electromagnetic parameter was determined using a vector network analyzer. Additionally, the thermal stability, thermal conductivity, phase change properties (latent heat and phase change temperature), and thermal reliability were analyzed using, TGA, thermal constant analyzer, DSC, and a programmable thermostatic tank.[55]

Table 3. Thermal analysis (TA) techniques with their related methods, abbreviation, and measured features of latent heat storage of PCMs.[48–52]

TA Measurement Technique	Method	Abbreviation	Output Property
Derivative thermogravimetry	Derivative thermogravimetric analysis	DTG	Rate of exchange of weight
Derivatography			A complex method in thermal analysis
Dielectric thermal analysis	Dielectric thermal analysis	DETA/DEA	Dielectric permittivity and loss factor
Differential scanning calorimetry	Differential scanning calorimetry	DSC	Heat flow difference
Differential thermometry	Differential thermal analysis	DTA	Change of temperature
Dilatometry	Dilatometer	DIL	Volume
Dynamic mechanical analysis	Dynamic mechanical analysis	DMA	Mechanical stiffness and damping
Emanation thermal analysis		ETA	Microstructure changes during heating of synthetic gibbsite
Exchanged/evolved gas measurement	Exchanged/evolved gas analysis	EGM/EGA	Gas exchange, gaseous decomposition products
Fast scanning calorimetry	Fast scanning calorimetry	FSC	The heating or cooling rate
Laser flash analysis		LFA	Thermal diffusivity and thermal conductivity
Themomechanometry	Thermomechanical analysis	TMA	Deformation, dimension
Thermally stimulated current			
Thermoacoustimetry	Thermoacoustimetric analysis	TAA	Acoustic properties
Thermoelectrometry	Thermoelectrical analysis	TEA	Electrical properties
Thermogravimetry	Thermogravimetric analysis	TGA	Change in weight/mass
Thermoluminescence		TL	Light emitted, oxidation
Thermomagnetometry	Thermomagnetic analysis	TM	Magnetic properties
Thermomanometry	Thermomanometric analysis		Pressure
Thermometric titration			Change of temperature
Thermoptimetry	Thermoptometric analysis	TOA	Optical properties, phase changes, surface reactions, color changes
Thermosonimetry		TS	Mechanical and chemical changes using sound

According to Chandel and Agarwal, in 2017, the following are the highlights and research gaps identified for TA evaluation. Most investigations relied on differential thermal analysis (DTA) and DSC procedures, whose findings varied depending on the mass studied, the cooling and melting rate, the flow rate of the inert gas passed, the homogeneity of the particles studied, and other factors. This makes it difficult to compare data from the literature. Besides, bulk materials' properties must be investigated in the context of how they will be employed in real-world applications. Additionally, the necessity for a complete material database for PCMs, as well as the creation of standards for describing PCM features, was highlighted in these studies.[5]

4. Safety Aspects of PCMs

Among LHS materials, organic TES substances are a fire risk due to their combustibility. Thermal oils are required to be used within specific safe temperature limits. Metals like sodium, potassium, etc. have a high fire risk. TES materials are usually safe and not toxic. However, thermal oils contain aromatic hydrocarbons. Similarly, formaldehyde used as a shell material in microencapsulation is a known toxin.[56] The study found that salt hydrates are non-toxic if handled properly, whereas commercial-grade paraffins, which are volatile and emit poisonous fumes, are a possible health threat and should be used with caution.[5]

4.1. The Environmental and Health Effects of Paraffin Wax

Food-grade candles (paraffin based) have been certified by the US Food and Drug Administration to apply in food, cosmetics, and medicine since they are considered non-toxic. Vinyl chloride and formaldehyde are volatile chemicals found in commercial-grade paraffin wax. Long-term exposure to their fumes might be harmful because of the presence of carcinogenic toluene and benzene components. If these materials are employed in structures, certain fire safety procedures are required. The United States Environmental Protection Agency [EPA] and the State of California have discovered seven or more significant toxins in paraffin wax, including naphthalene, toluene, benzene, and methyl ethyl ketone. Because they are non-biodegradable and non-renewable, their disposal is an environmental concern.[5]

4.2. The Environmental Effect of Salt Hydrates, and its Long-Term Health Implications

Glauber's salt is normally a non-toxic salt hydrate, however, it should be handled with caution since its dust can cause asthma attacks and eye irritation.[57] When calcium chloride hexahydrate ($CaCl_2H_{12}O_6$) is consumed, it causes serious health problems as well as eye discomfort. If it comes into contact with the skin, it might cause inflammation. It can potentially cause serious respiratory issues. As a result, it should be handled with caution.[58] According to the results of animal tests,

Table 4. Summarizes the safety aspects of several PCMs.[5,11]

PCMs	Health hazards/Toxicity/Environmental Impacts
Fatty acids	Variable toxicity
Vegetable oils	Safe when ingested; food-grade; highly flammable; renewable; carbon-free; environmentally friendly
Salt hydrates	Usually not flammable, varying grades of toxicity, magnesium chloride ($MgCl_2$ $6H_2O$)- non-toxic, can irritate the eyes and skin; calcium chloride ($CaCl_2$ $6H_2O$)- eye irritant, health hazard when swallowed; magnesium nitrate ($MgNO_3$)- non-biodegradable and safe; Glauber's salt- dust can cause asthma and eye irritation
Paraffin wax	Non-biodegradable; flammable carcinogenic; when commercial wax is burned, it produces harmful toxins
Eutectic	It is dependent on the eutectic components, that is, if it is an inorganic or organic mixture

sodium carbonate (Na_2CO_3) appears to be safe and non-toxic. However, inflammation of the throat and mouth is probable.[59] Magnesium nitrate ($Mg(NO_3)_2(H_2O)_x$) has not been shown to be hazardous or irritating to the eyes, and it is also innocuous for the skin, non-carcinogenic, and has not been proven to have any negative effects after prolonged exposure to its fumes. However, it is not biodegradable.[60] Although magnesium chloride hexahydrate ($MgCl_2$ $6H_2O$) has not been determined to be a health danger and may be readily eliminated from the body if consumed, it can cause skin and eye irritation as well as respiratory issues. The toxicity of different salt hydrates varies. Although they are normally non-toxic, they can cause skin irritation, eye discomfort, and respiratory difficulties.[61] If there is any human contact with the salts, it's a good idea to read the data sheets thoroughly to guarantee safety.[5] The safety aspects (health hazard, toxicity, and environmental impact) of various PCM types are summarized in **Table 4**.

5. Applications of PCMs in Life Science

Thermal energy stored may be employed for cooling and heating purposes, and there is a lot of room available to create new technologies and techniques to optimize and improve it. Exploring diverse thermal storage materials and technologies for varied applications opens up a plethora of possibilities for the long-term development and exploitation of thermal energy.[14] The life science applications of PCMs are discussed in this section (**Figure 3**).

5.1. Biological Applications

Recently, the unique heat absorption and heat-releasing capabilities of PCMs led to their use in a variety of biological applications. It is pivotal to convert PCMs into colloidal particles with consistent sizes and theranostic agents when using them in biomedical research. Additionally, processing PCMs as stable colloidal particles in an aqueous medium under physiological conditions is critical for using them in nanomedicine.[17] PCMs' latent heat permits them to release or absorb heat for extended periods of time, which is beneficial in a variety of medical therapies, for instance, buruli ulcer treatment, thermotherapy, arthritis treatment, portable eye masks, medical dressing, thermal ablation/thermal tumor ablation, and drug delivery applications.[62–65] The heat that penetrates deeply into the muscles promotes blood flow, eliminates harmful toxins, and muscular relaxation. Natural fibers are environmentally friendly, renewable, and biocompatible. The use of bio-based materials as phase change microcapsule shell materials has been studied by several scientists. Some researchers have employed regenerated silk fibroin as an encapsulation substance to produce phase change microcapsules because it has high reproducibility and biocompatibility.[63,66]

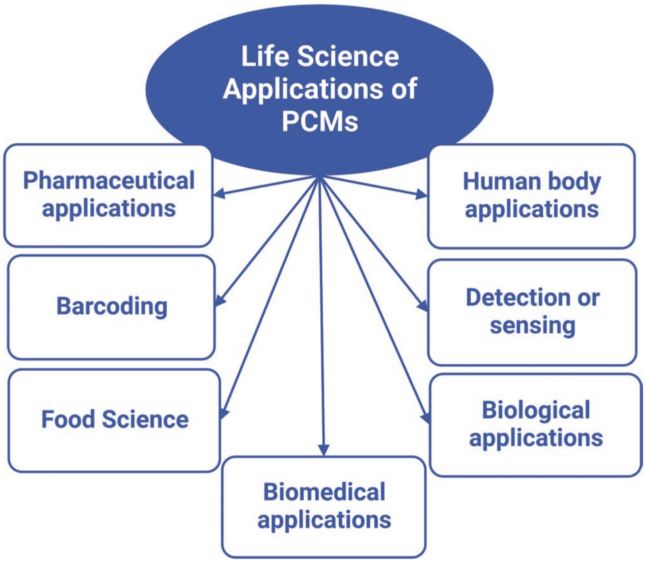

Figure 3. Illustrates the life science applications of PCMs.

These materials are not popular due to their high cost and lack of knowledge, but there is potential to make them more dependable, cost-effective, and efficient.[67] The World Health Organization (WHO) is encouraging researchers to find cost-effective solutions for preserving heat-sensitive medications for extended periods of time at a safe temperature. This may be accomplished by making use of PCM's heat-storing and releasing capabilities.[68]

5.2. Biomedical Applications

Biomedical applications include applications to the human body as well as cold chain and logistics involving transportation and storage. Medical applications, have a distinct emphasis and set of needs, and hence may be considered a different market.

In general, cold or heat treatment, such as reusable cooling packs employed after sporting stress, surgery, accidents, heat pillows for rheumatism or physiotherapy, and blankets to prevent hypothermia are all examples of applications to the human body. Specific uses for babies include incubators, heaters, and coolers. Another use is to make orthoses and prostheses more comfortable to wear by using the PCM to minimize sweat where the orthosis or prosthesis and limb are linked.[35] The Outlast PCM in the Alpha SmartTemp Liner stores and absorbs heat as it builds up in a residual limb, preventing the development of perspiration. The liner stabilizes skin temperature by releasing stored heat when the body cools, keeping an amputee comfortable.[69,70]

Polyethylene glycol (PEG) treated textiles with liquid transport and antimicrobial qualities are able to be used for medical applications for instance incontinence products, surgical gauzes, and diapers. Thermo-controlled fabrics with PCM can keep the temperature within a certain range, making them suitable for clothing and heat-cool treatments. Molecular alloys are materials with a high latent heat of fusion that may be employed to store thermal energy.[71] Mondieig et al., (2003)[72] described some molecular alloys that were used in medical applications, for example, material alloy PCM used in double-walled pouch packaging for blood thermal protection. D.E. Santis, in 2006[73] noted the fact that PCM has strong thermo-regulating characteristics. It's critical to control heat during the phase transition of PMMA/PCM for in situ polymerization and inserted bone cement since increasing the temperature during the exothermic reaction of the injected material might kill most of the nearby host tissue. To improve the thermo-mechanical properties of PCMs, micro-capsulated paraffin was incorporated into the PMMA matrix.

Asphyxia and oxygen deprivation during birth can cause brain damage in newborns. In the temperature gap required for cooling newborns suffering from oxygen deprivation during delivery or within 6 h, Glauber salt solution can serve as a medically suitable phase transition material. The infant's rectal temperature should be maintained at 33–34±0.5 °C with this Glauber salt combination with sulfate anhydrites. Olson et al., (2021) reported the Glauber salt solution is a therapeutically appropriate PCM in the temperature interval required for cooling asphyxiated newborns.[74]

PCMs utilized in biological applications often have high latent heat of fusion and low melting temperatures. From the standpoint of melting point and high latent heat of fusion, the FAs acetamide (AC), stearic acid (SA), palmitic acid (PA), myristic acid (MA), capric acid (CA), and lauric acid (LA), are prospective, plentiful, and economical materials for thermal usage. **Table 5** briefly summarizes the features of some of the current and newly developed PCMs for biomedical applications studied.[67]

Table 5. Properties and potential biomedical applications of PCMs.

	Medical application	Temperature range/required temperature/[°C]	Phase change materials	Latent heat of fusion [J g^{-1}]	Melting temperature [°C]
Heating	Thermotherapy of Buruli Ulcer	42–46	Sodium acetate trihydrate	264.00	58.00
	Pads for orthopedic applications	42–46	Dodecanoic Acid (Known as Lauric Acid)	190.21	46.13
	Pads for back pain	42–46	Sodium thiosulfate ($Na_2S_2O_3$ $5H_2O$)	176.65	48.50
			Camphene	264–289 150.41	44–48
			LA-MA (20/80 wt.%)*	176.73	48.27
			MA-SA(50/50 wt.%)*	183.69	46.82
			MA-PA(60/40 wt.%)*	145.43	48.29
			LA-PA (50/50 wt.%)*	193.10	41.30
			LA-AC (90/10 wt.%)*		41.25
Cooling	Pads for back pain	10–20	Paraffin C16-C18,	152.00	20–22
			Polyethylene Glycol 600	127.20	20–25
			CA-LA (80/20 wt.%)*	136.91	21.24
			CA-MA (90/10 wt.%)*	135.84	22.63
			LA-CA-MA-SA (20/30/30/20)*	125.08	15.15
	Transportation of vaccines and other medicines	2–8	Paraffin C14	165.00	4.50
			Paraffin C15-C16	153.00	8.00
			Polyglycol E400	99.60	8.00
Heating/cooling	Maintaining clinical sample temperature	35–40	Paraffin Wax	222–246 190.21	36–38
			Lauric Acid	264.00	46.13
			Sodium dihydrogen phosphate	146.90	35.50
			dodecahydrate (Na_2HPO_4 $12H_2O$)	218.54	36.10
			Zinc nitrate hexahydrate ($Zn(NO_3)_2$ $6H_2O$)	172.80	34.59
			LA-SA (60/40 wt.%)*	171.96	37.58
			LA-MA (60/40 wt.%)*		36.22
			LA-MA (70/30 wt.%)*		
	Clinical bed/for surgical dress	30–35	Calcium chloride hexahydrate ($CaCl_2$ $6H_2O$)	190.80	29.00
			Sodium sulfate decahydrate (Na_2SO_4 $10H_2O$)	254.00	32.40
			CA-AC (60/40 wt.%)*	153.96	32.86
			CA-AC (70/30 wt.%)*	160.53	30.49
			CA-SA (90/10 wt.%)*	160.39	29.54

*Phase change materials developed at Non-conventional Energy Laboratory and tested through differential scanning calorimetry. Capric acid (CA), lauric acid (LA), myristic acid (MA), palmitic acid (PA), stearic acid (SA) and acetamide (AC).

5.3. Drug Delivery and Controlled Release Applications

The ability to manage drug distribution in place and time is the goal of a drug delivery system. Recently PCMs have been studied in drug delivery systems to treat cancer, for instance, photodynamic therapy, thermal treatment, chemotherapy, and a combination of several treatments. PCMs in a drug delivery system can precisely regulate drug release, inhibit the leaking of medications before they arrive at the target site, improve the therapeutic impact, and keep the system running smoothly.[71,75] PCMs are used as "gatekeepers" in the synthesis of a PCM-based drug delivery system, which means the switch is a response to the temperature, and an acousto-thermal conversion agent, magnetic-thermal conversion agent, and photo-thermal conversion agent, are added, resulting in a nanoscale release system. Metal nanoparticles, carbon nanoparticles, and other energy conversion agents are ubiquitous, with gold nanoparticles attracting particular attention due to their high energy conversion efficacy and biocompatibility.[63] Chen et al., (2020) developed biodegradable hollow mesoporous organosilica-based nanosystems with dual stimuli-responsive drug delivery for efficient tumor inhibition by synergistic chemo- and photothermal therapy (PTT). To construct a multifunctional nanosystem, with stimuli-responsive drug delivery, copper sulfide (CuS) nanocrystal was used in the system as a photothermal agent, and PCM as a stimuli-responsive "'gate-keeper"' into the biodegradable hollow mesoporous organosilica nanoparticles (HMONs). The capping of PCM on HMONs enables the temperature-responsive drug release manner, drug delivery leakage prevention, and the reducing-responsive biodegradability of disulfide-hybridized HMONs permit the tumor microenvironment-sensitive drug release. With the help of the near-infrared-thermal conversion of CuS nanocrystal, the fabricated nanocarriers could realize both the external and endogenous stimuli -triggered drug release and achieve the synergistic effect of chemo- and photothermal treatment for inhibition of tumor. Therefore, the effective delivery of doxorubicin (DOX) and precise drug release at the tumor site occurred. (**Figure 4**)[76]

PCMs can also act as heat buffers in the drug delivery system. The temperature of the treated tissue must be kept within the optimal range during thermotherapy. If the temperature is very low, the thermotherapy impact will not be reached. The surrounding healthy tissues will be destroyed if the temperature is too high. PCMs may be used to control the temperature in a number of ways. As a result, a PCM-based drug delivery system offers a lot of promise for boosting chemotherapeutic efficacy, lowering side effects, and increasing biosafety.

Mesoporous composites' size and porosity play significant roles in determining their loading and characteristics, and their thermodynamic properties frequently exhibit considerable scale dependency.[77] Mesoporous silica materials are effective PCM carriers in drug delivery systems that possess high specific surface area, biocompatibility, low toxicity, corrosion resistance, customizable size, and changeable surface shape. A photothermal conversion agent can also be loaded into the hollow structure of mesoporous silica. Poudel et al., in 2018 created hollow silver gold nanoshells (HSGNS) in a hollow mesoporous silica shell allowing pharmaceuticals to be loaded not only in the mesoporous silica but also in the HSGNS (**Figure 5**). The mesopore was blocked with PCM lauric acid after loading the medication 5-fluorouracil to construct a drug

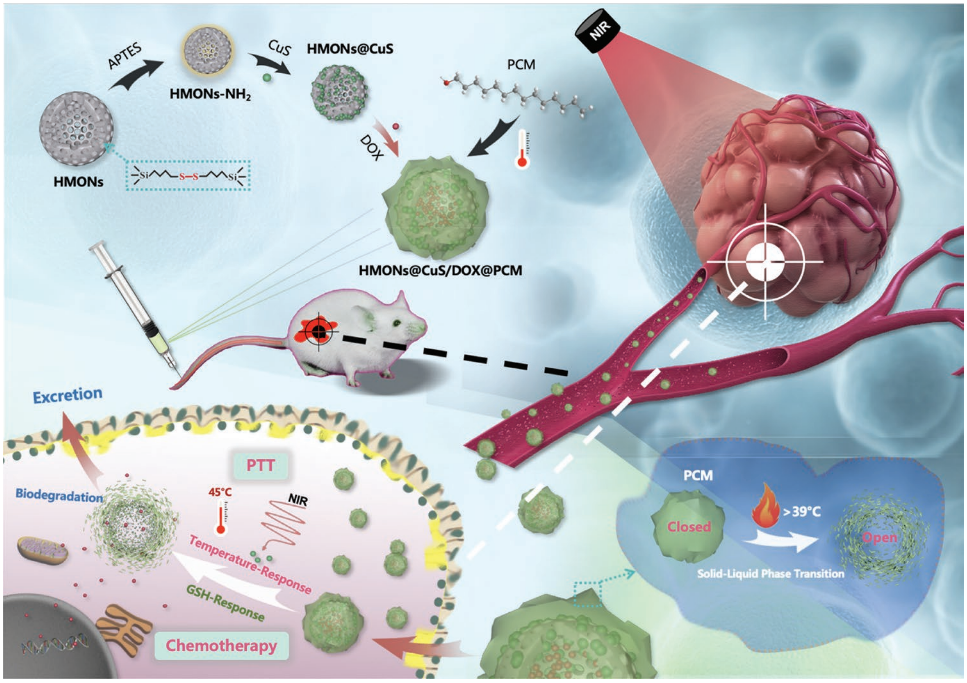

Figure 4. Represents the synthesis of PCM-DOX/HMONs-CuS nanodevice with dual stimuli-responsive drug release for synergistic chemo- and photothermal cancer treatment. Hollow mesoporous organosilica nanoparticles (HMONs), copper sulfide (CuS), doxorubicin (DOX), 3-aminopropyltriethoxysilane (APTES), glutathione (GSH), near-infrared (NIR), PTT. Reproduced with permission.[76] Copyright 2020, Elsevier.

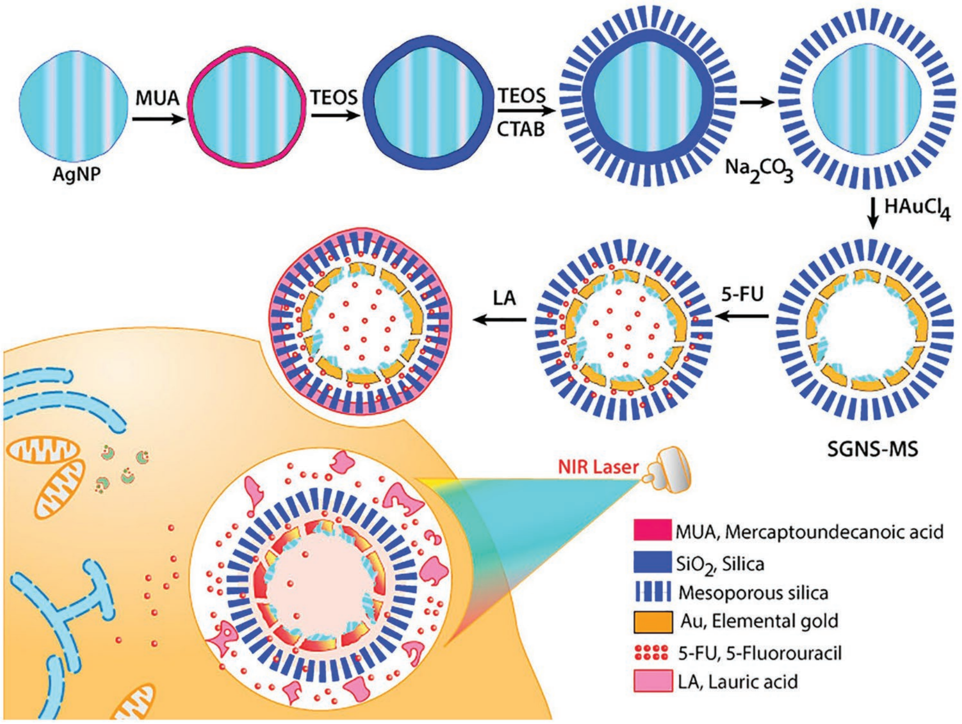

Figure 5. Schematic diagram showing in situ fabrication of anticancer drug 5-fluorouracil loaded hollow silver-gold nanoshells-mesoporous silica-lauric acid through galvanic reaction. Lauric acid, LA; 5- fluorouracil, 5-F; Gold tetrachloroauric acid, HAuCl$_4$; elemental gold, Au; sodium carbonate, Na$_2$CO$_3$; tetraethyl orthosilicate, mesoporous silica-coated silver-gold nanoshells, SGNS-MS; cetyltrimethyl ammonium bromide, CTAB; TEOS; 11-mercaptoundecanoic acid, MUA; Silver nanoparticles, Ag NPs. Reproduced with permission.[78] Copyright 2018, Elsevier.

delivery system for prostate cancer therapy. The high-powered laser can directly destroy the cancer cell by laser irradiation via photothermal effect. Therefore, the introduced system provided efficient chemo- and PTT.[78]

Figure 6a,b illustrates temperature-controlled release of homogenous PCM (1-tetradecanol, m.p. 38–39 °C) beads containing gelatin coated with an organic dye. The particles holding the medications leached out of the melted PCM matrix above the melting points of the PCMs (about 60 °C), and the pharmaceuticals could then be released from the colloidal particles, as illustrated in Figure 6c. Even at 37 °C, which is equivalent to the human body's temperature, this temperature control was achieved. It was also possible to release the organic dye from hollow polymer particles in a controlled way at 39 °C utilizing a binary combination of PCMs (1-tetradecanol and lauric acid) with variable melting points to change the PCMs' melting behavior (**Figure 7**). In small doses, lauric acid and 1-tetradecanol, are recognized with low toxicity because they are originally derived from natural fats and oils and thus are often used as ingredients for food and pharmaceuticals. There were no fatalities or substantial gross lesions at necropsy when rats were given dosages of up to 10 g kg^{-1} of lauric acid via gavage. Although the minimum fatal or poisonous dosage of 1-tertadecanol has not been determined, the acute lethal dose in an adult human case is predicted to be 80–200 g based on rat research. These findings show that lauric acid with a melting point of 43–46 °C and 1-tetradecanol with a melting point of 38–39 °C should be appropriate candidates in a thermally controlled medication delivery system.[79,80]

Lasered graphene microheaters modified with a combination of paraffin wax and O,O′-bis(2-aminopropyl) polypropylene glycol–block–polyethylene glycol–block–polypropylene glycol for smart patch drug delivery were developed (**Figure 8**). This study exhibits a new strategy for a smart patch through which release can be controlled, permitting repetitive dosing. Instead of depending on passive diffusion, delivery is initiated and stopped by controlled heating of the PCM with transfer only happening when the PCM transitions from solid to liquid.[81]

Only some inorganic salts such as Ca(NO3)2·4H2O (with a melting point of 47 °C), and organic compounds like Paraffin C23 (melting point of 47.5 °C) have the melting point slightly above the body temperature which can be applied for controlled release and biomedical application, but due to the biosafety concern or engineering difficulties has never been successful in in vivo and/or practical studies. Xia et al., (2020), in their review article specifically focused on fatty alcohols and FAs for developing a controlled release system based on PCMs for drug delivery and related applications. FAs/alcohols with different chain lengths or using their eutectic mixtures can obtain a PMC with a melting point near our body temperature, to enable them for practical application. The PCM can be used as a filling or cork for hollow micro, and nanoparticles to provide an "on-off" control on the payload release. Recently, PCMs have been developed for the encapsulation and delivery of inorganic irons (e.g., SeO_{3-2} and Ca^{2+}), anticancer drugs (e.g., DOX and paclitaxel), biomacromolecules (e.g., nerve growth factors), reactive species (e.g., 2,2′-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride and diethylenetriamine diazeniumdiolate), and

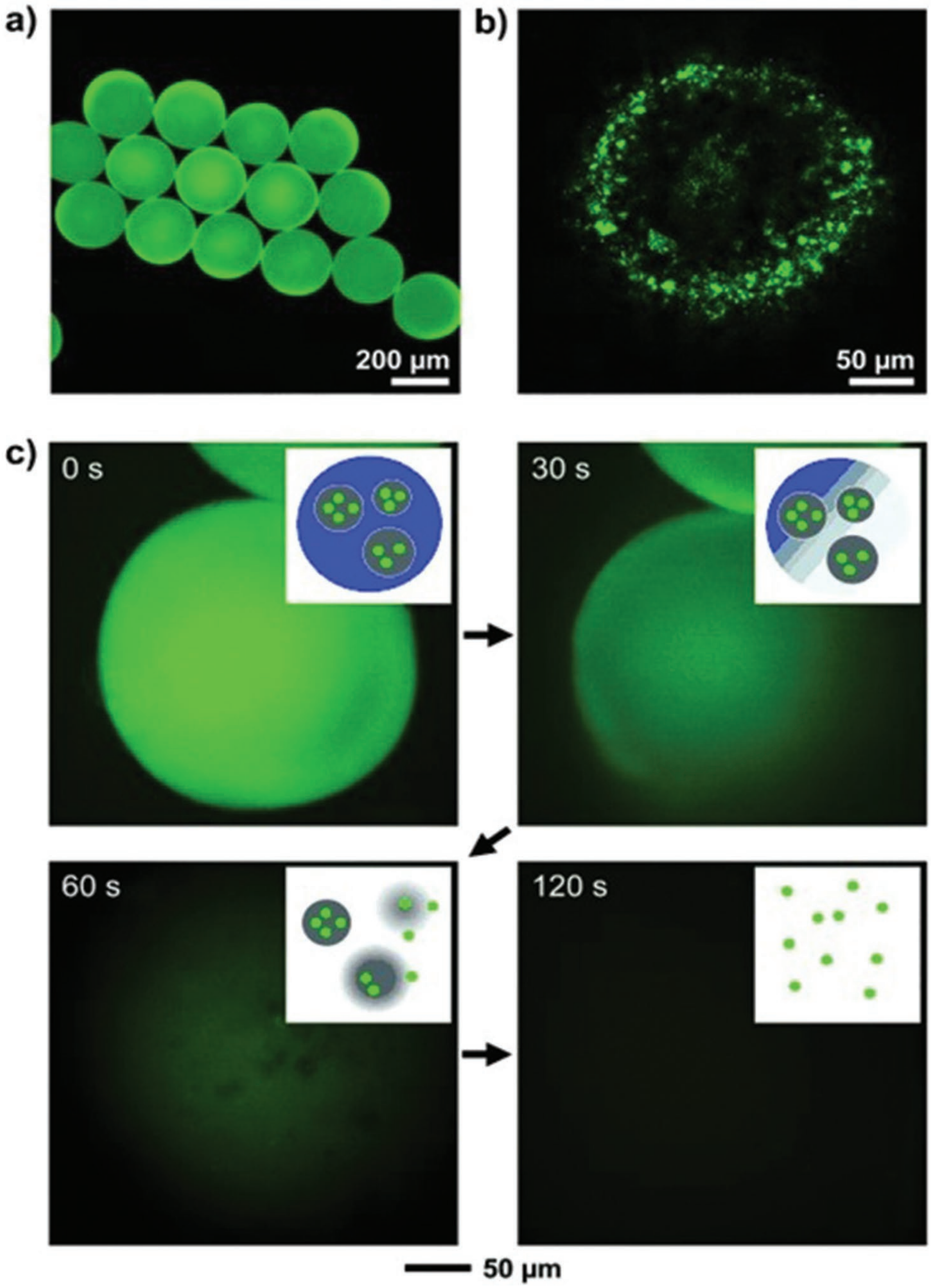

Figure 6. a) Fluorescence, b) confocal micrographs of PCMs spheres with fluorescein isothiocyanate-dextran-loaded particles of gelatin. c) Micrographs of time-lapse fluorescence displaying the melting of the PCMs sphere and the dye release from the gelatin when the temperature was raised over the PCMs melting temperature. The three key phases for dye release are shown in the insets: melting sphere particles of PCMs, leaching out of particles of gelatin, and release of dye when gelatin dissolves. Reproduced with permission.[80] Copyright 2010, Wiley-VCH GmbH.

nanoparticles (e.g., Fe_3O_4, MnO_2, and gelatine). Additionally, natural FAs and fatty alcohols display a more promising future due to their low cost, abundance, diversity, biodegradability, low toxicity, and natural bioavailability.[17] Xu et al., (2022) used a eutectic mixture of lauric acid and stearic acid at the weight ratio of 4:1 as a thermoresponsive PCMs with the phase transition temperature in the developed methylglyoxal (MGO)-activatable second near-infrared (NIR-II) fluorescence phototheranostics. These PCMs were engineered for hyperthermia-triggered spatiotemporally tunable drug release. They demonstrated that the NIR-II fluorescence nanotheranostics is specifically activated in the tumor and efficiently suppressed 4T1 breast tumor growth in mouse model. The NIR-II fluorescence imaging-based nanotheranostics might imply novel insight into reactive metabolite-activatable precise therapy of tumor.[82] Xue et al., (2020) introduced a size-tunable photomask to enable the delivery of biological effectors (nerve growth factor and epidermal growth factor) in an on-demand and spatiotemporally

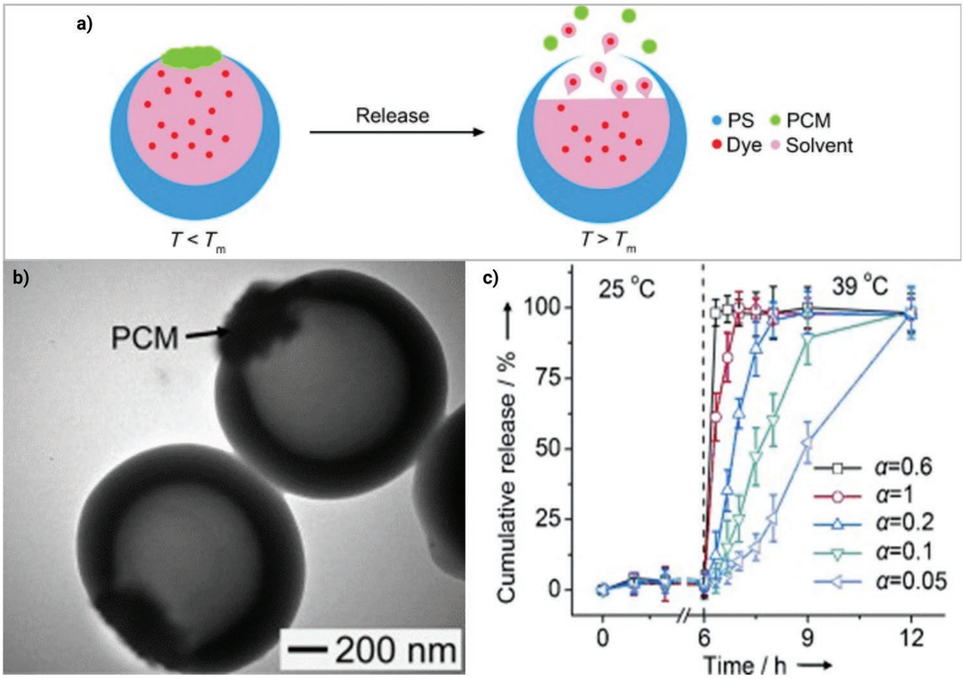

Figure 7. a) Dye release from a polymeric hollow particle with a PCM corked surface hole. b) Transmission electron microscopy pictures revealing 1-tetradecanol-corked particles. c) Rhodamine B release profiles from particles covered by a binary combination of PCMs containing 1-tetradecanol and lauric acid in a pH 7.4 buffer solution. To alter the PCMs melting temperature, the volumetric ratio (α) of 1-tetradecanol to lauric acid was changed from 0.05:1 to 1:1. polystyrene (PS), melting temperature (T_m), and PCMs. Reproduced with permission.[79] Copyright 2013, Wiley-VCH GmbH.

controlled manner. They designed a sandwich-type scaffold containing PCM microparticles between two layers of electrospun fiber. They fabricated electrospun fiber using a 10 wt.% polycaprolactone solution in a mixture of dichloromethane and dimethyl. They co-loaded the biological factors with a photothermal dye (indocyanine green) in the PCM microparticles. They manipulated the spatiotemporal distributions of the biological effectors with the use of a tunable photomask and investigated the migration of NIH-3T3 fibroblasts on the scaffold under the masked, photo-triggered release of EGF. The results displayed acceleration in the directional migration of NIH-3T3 fibroblasts along the uniaxial or radial direction of fiber

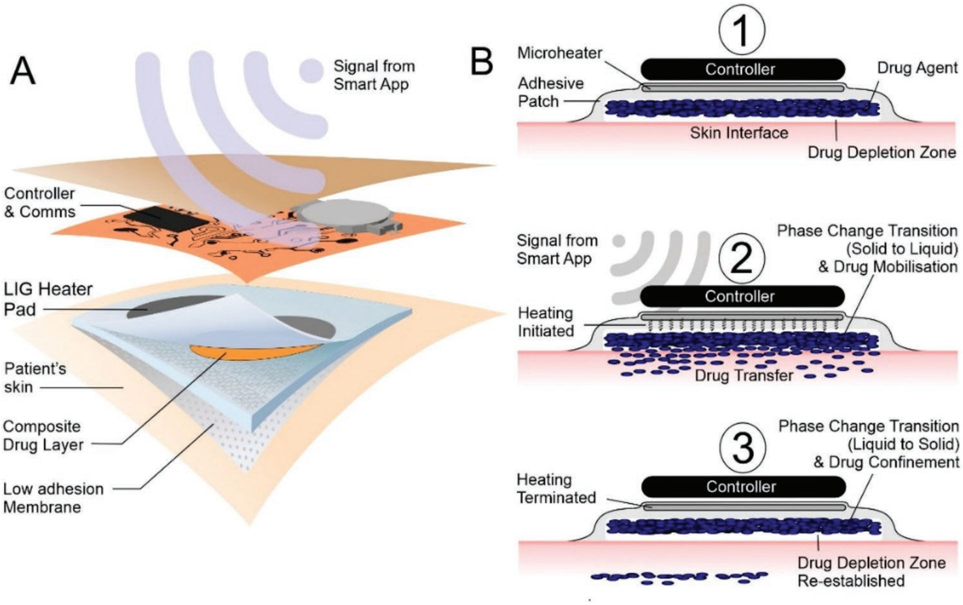

Figure 8. a) Represents a schematic illustration of the patch before activation, without skin contact, and the drug is immobile, b) activation starts the heating cycle, and mobilizes the drug to the surface of the skin, and the system cools and the phase change reoccurs and the drug process becomes immobile again. Reproduced with permission.[81]

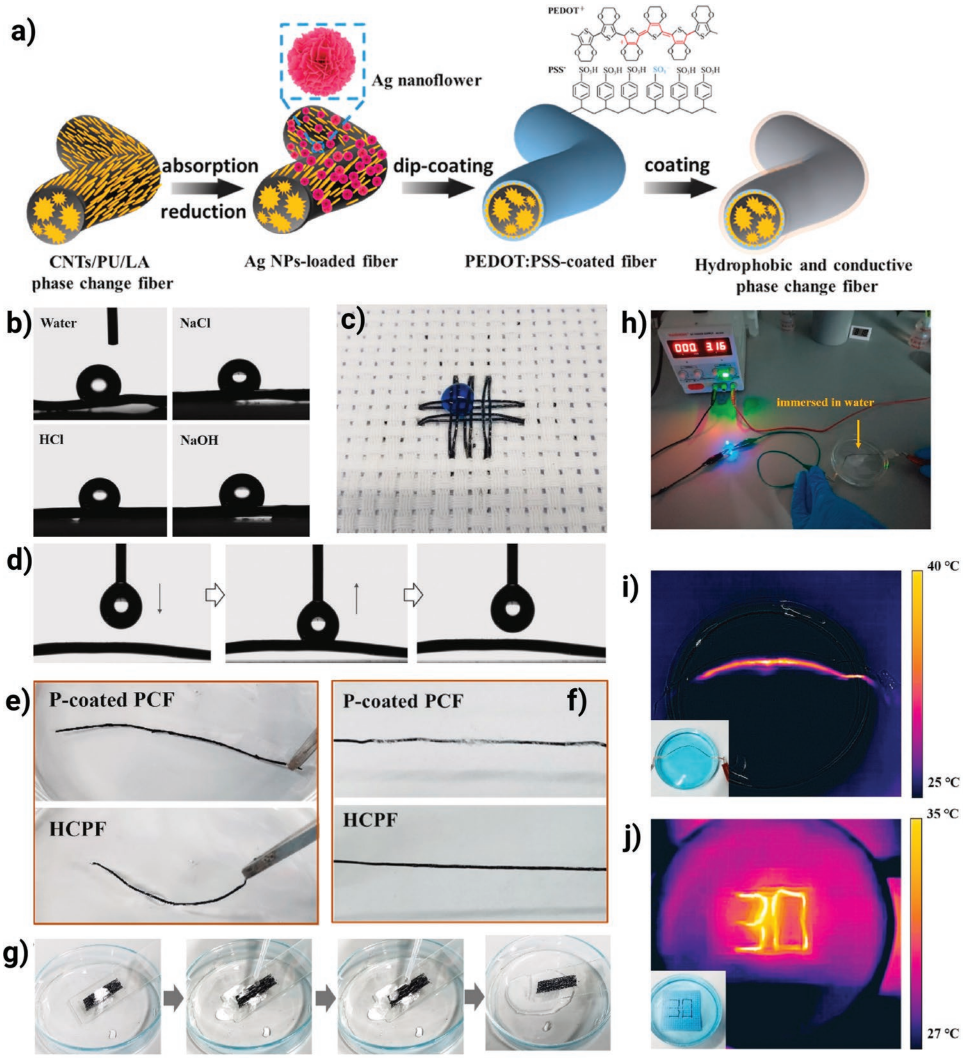

Figure 9. a) Represents the design of the multi-stimuli responsive hydrophobic conductive phase change fiber for thermal/photo energy storage and harvesting. b) Contact angle measurement of hydrophobic phase change fiber with NaCl (10 wt.%), NaOH (1 M), water and HCl (1 M), solution droplets, c) Illustrates dyed water droplets on woven fabric, d) Exhibit the water droplet with the hydrophobic phase change fiber, e) Repelling water, f,g) self-cleaning features, h) the LED circuit, picture and IR image of fiber under i) voltage of 20 V and j) sunlight irradiation under water. Reproduced with permission.[89] Copyright 2022, Elsevier.

alignment by controlling the release of the epidermal growth factor. This approach can be extended to other types of scaffolds (e.g., hydrogels and 3D porous sponges), as long as the PCM microparticles loaded with biological effectors can be integrated into the scaffold and the NIR light can penetrate through and reach the microparticles.[83]

5.4. Human Body Applications

The human body applications of PCMs are explored in this section. Any application that comes into contact with the human body to maintain it in a comfortable normal body temperature range, or even to keep it alive, is referred to as a life science application. A PCM absorbs or releases heat according to its phase, allowing it to manage the exchange of heat among the body and its immediate surroundings. Daily clothing, sleeping equipment, and protective garments are the most common life science applications. In this section, biomedical applications are explored because biomedical usage typically possesses different markets and requirements.[35]

Clothing; during activities, the PCM in the clothing absorbs, and releases heat based on the temperature of the body and the surrounding environment, enhancing comfort by preventing freezing and sweating. It is usual to utilize a microencapsulated, organic PCM for simple incorporation into everyday clothing. The microencapsulated PCM may then be used in coatings or incorporated into fibers, which can subsequently be used in a variety of ways in a variety of clothing. Commercial items in this field of application have been available for many years and are well established, ranging from undergarments for coats, gloves, caps, and even helmets and shoes; see, for example.[84] Schoeller Textil AG and Microtek Laboratories Inc. are the dominant companies engaged in this market.[85,86]

Protective garments are designed for a wide range of activities and environments, including protection against cooling or overheating of the body during higher physical activity such as during hard work, when exposed to extreme cold or heat temperature, such as outdoors, but also when other protective gear makes temperature regulation difficult, such as personal protective equipment worn by firefighters or medical personnel in an unsafe situation. Since it is used for protection, it is common practice to try to optimize the PCM's impact and its duration. As a result, relatively significant volumes of PCM are used, generally in the form of pouches containing organic or inorganic PCMs. Industrial workers, athletes, firefighters, and medical staff can all benefit from such vests.[35]

In textile industries, in the early 1980s, NASA pioneered the process of incorporating PCM microcapsules into fibers to advance the thermal barrier features of garment materials, especially space suits. PCMs, such as nonadecane, have been encapsulated in the fabrics to reduce the impact of extreme temperature variations on astronauts during space missions.[87] The flexible, stretchable smart conductive textile was fabricated through electrospinning of a solution of thermoplastic polyurethane (PU)/lauric acid (LA)/multiwalled carbon nanotubes (MWCNTs) and dip-coating conductive polymer poly(styrenesulfonate): poly(3,4-ethylenedioxythiophene) (PSS: PEDOT) on the obtained nanofibers. The intelligent fabric exhibited phase change enthalpy and tunable temperature that respond to external stimuli such as sunlight, infrared light, and electrical voltage which have the storage and conversion of energy reversibly with high efficiency.[88] In another study, smart flexible electro-/photo-driven energy storage fiber with self-cleaning, outstanding hydrophobicity, electrical conductivity, tunable phase change temperature, high enthalpy, and extra shape stability was fabricated by the wet spinning method. The phase change fiber was fabricated using carbon nanotube/polyurethane/lauric acid and loaded with silver nanoflowers and coated with poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) (**Figure 9**). The prepared fiber was coated with hydrophobic fluorocarbon resin to ensure the safety of the materials to external environment.[89] Zhang et al., (2021) reported a stress-sensitive, superelastic PCM with the potential for TES temperature control, and stress induction using polyacrylamide-based hydrophobically associated hydrogel/PEG with an ultimate tensile ratio greater than 500% through molecular self-assembly technology.[90]

5.5. Barcoding

An ultrahigh capacity coding system with compact dimensions is required to recognize each object in a large group of objects. Optical barcodes, radio-frequency identification (RFID) chips, and microfibers are routinely used to identify and code a variety of things, however, no existing technology can affordably barcode a large number of small things. During a linear thermal scan, the distinct sharp melting temperature associated with metal-based PCM nanosize particles are ideal for barcoding.[91,92] The melting characteristics of metal PCMs may be used to generate mixtures with distinct DSC signatures (Figure 9). The encoding potential is proportional to the number of melting temperatures or nanosize particle structures, assuming that each melting temperature does not overlap and is sufficiently sharp. The number of distinct barcodes will be 2n1, where n is the total number of melting peaks, as calculated by Yang Hui's triangle (1238–1298) or Pascal's triangle (1653). Ma and colleagues showed that utilizing ten distinct PCM particles yielded more than 1000 potential barcodes while using 50 different constituents yielded 10^{15} possible barcodes, which is sufficient for most identification needs. Naturally, the requirement for a high number of PCM constituents with separate melting points poses a problem, namely, producing 50 individual PCM substances with a distinct melting point that do not interact with each other or the matrix in which they are embedded. However, it has been proved that a mixture of four PCM particles may be implanted in aluminum and accurately identified depending on the particle ratio. Each melting peak in the four-element system can be designated as zero or one based on whether the heat flow is more than or less than a threshold value (**Figure 10**). 0000, 1000, 0100, 0010, 0001, 1100, 1010, 1001, 0110, 0101, 0011, 0111, 1001, 1101, 1011, and 1111 are the 16 combinations of four elements. This application has the possibility to revolutionize the nature of identifying systems as we know them, and it might be extremely useful to law enforcement officers. For example, ubiquitous tagging will make it easier to detect items that were previously difficult to track.[93]

5.6. Detection or Sensing

The range of biomarker concentrations, the fact that sole biomarkers cannot reliably discriminate indolent and lethal cancers, and the absence of diversity (i.e., immediate recognition of various signals) in presently employed methods are all issues that plague the use of biomarkers in the detection of cancer.[94] Su and colleagues created a PCM-based system for simultaneous detection of several biomarkers by using the strong melting peaks provided by PCMs on DSC as thermal fingerprints.[91] Varying PCM particles have dissimilar melting values, but they all respond to extremely modest temperature changes.[32] The temperature range of standard thermal assessment equipment is 100–700 °C, and numerous PCM materials may be set to a peak width of 0.6 °C for a given ramp rate, implying that there might be 1000 possible melting points. Employing a cocktail of materials with discrete biomarker specificity and DSC peaks, many biomarkers may be recognized at the same time (**Figure 11**) by changing materials with ligands unique to a specific biomarker. Because this method relies exclusively on the melting temperature, it is unaffected by turbidity in the solution, as well as the existence of colorful molecules, salts, or conductive substances. Su and co-workers utilized this technology to properly identify two distinct deoxyribonucleic acid (DNA) biomarkers with a concentration difference of three orders of magnitude (100 nM and 100 pM), demonstrating multiplicity over an 11-order-of-magnitude concentration range. In the future, this technology of thermally detecting numerous biomarkers might be a critical tool in cancer diagnosis.[32,91,94]

An intelligent electrochemical biosensing system for improving dopamine detection was developed by the integration

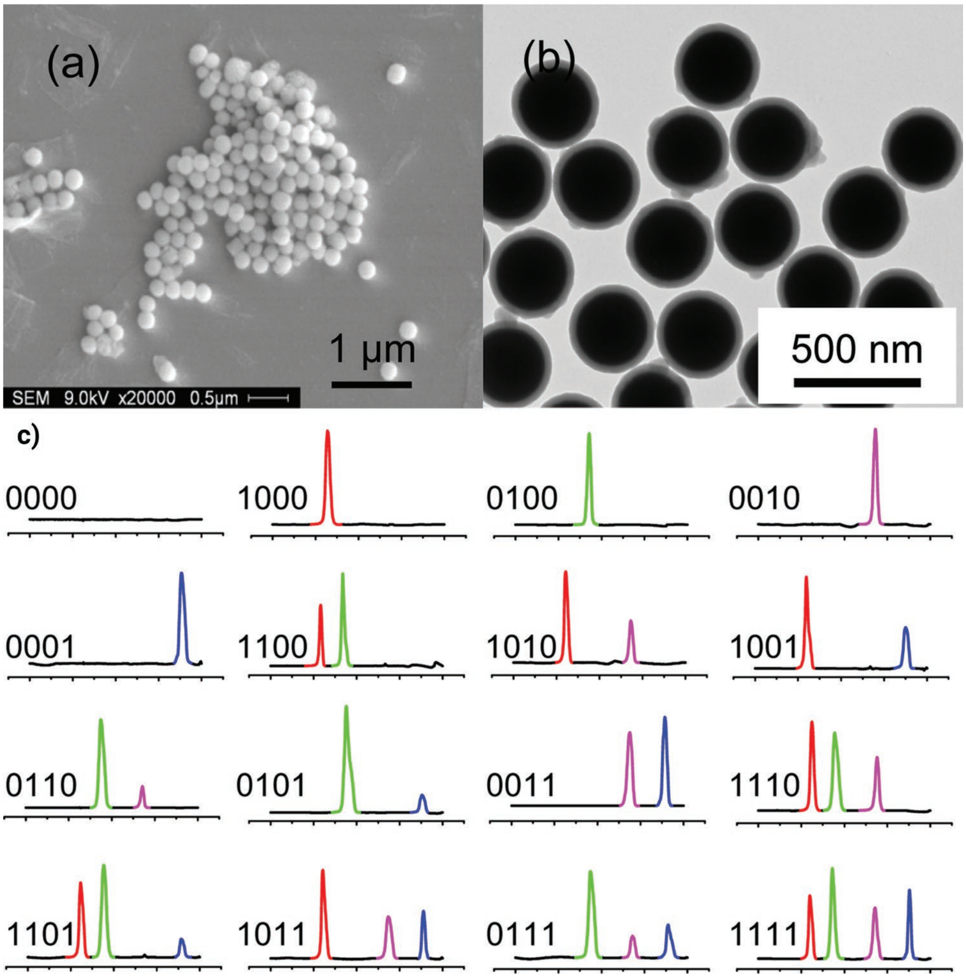

Figure 10. PCM nanoparticles are used for barcoding. a,b) Transmission electron microscopy and scanning electron microscope pictures of Bi particles enclosed in silica shells for barcoding use. Reproduced with permission.[32] c) Thermal barcodes made with four distinct nanoparticle ratios: bismuth, tin, lead-tin alloy, and indium. The curves of differential scanning calorimetry (DSC) were observed at temperatures ranging from 100 to 300 °C. Each number refers to a distinct tag made up of four separate PCMs with varying melting temperatures (There are a total of 16 potential combinations). Reproduced with permission.[93]

of a paraffin-based phase change microcapsule (polypyrrole/SiO2) with a zeolite imidazolate framework-8 with a thermal self-regulation function. The spherical core-shell microstructure displayed an effective temperature-regulation capacity with enhanced enzymatic bioactivity, good thermal stability, and thermal impact resistance. The enhancement of the sensor was due to in situ thermal management derived from its PCM core of the electroactive microcapsule.[95] In another study, an intelligent glucose biosensor was designed by microencapsulating *n*-docosane in SiO_2, and depositing polydopamine/carbon nanotube as an electroactive layer to detect glucose at high temperatures. The authors evaluated the thermal characteristics temperature at a maximum degradation rate using a differential thermogravimetric (DTG) thermogram that reflects the thermal stability of a material.[96] These studies propose strategies for designing and fabricating thermal self-regulating intelligent biosensors with improved determination capabilities to detect a variety of chemical compounds in a wide range of applicable temperatures. Temperature has a direct impact on how effectively enzymes catalyze reactions. Therefore, microencapsulation of PCMs can increase the ability of an enzyme to be detected at high temperatures by achieving the function of thermal control in addition to preventing enzyme leakage (**Figure 12**).[96,97]

In the pharmaceutical industry, Tetracycline is an important antibiotic that has been used widely and can enter the environment through various routes. It can be accumulated in the food chain, natural water system, soils, etc. Therefore, it is important to detect Tetracycline in minor amounts. Yu et al. developed a fluorescent sensing system based on molecularly imprinted phase-change microcapsules and carbon quantum dots for high-efficient detection of tetracycline in harsh temperature conditions.[98]

5.7. Food Science and Agricultural Applications

To maintain food quality and microbial food safety some foodstuffs must be distributed and marketed under refrigeration/chilling or freezing conditions. It is critical to avoid food spoilage,

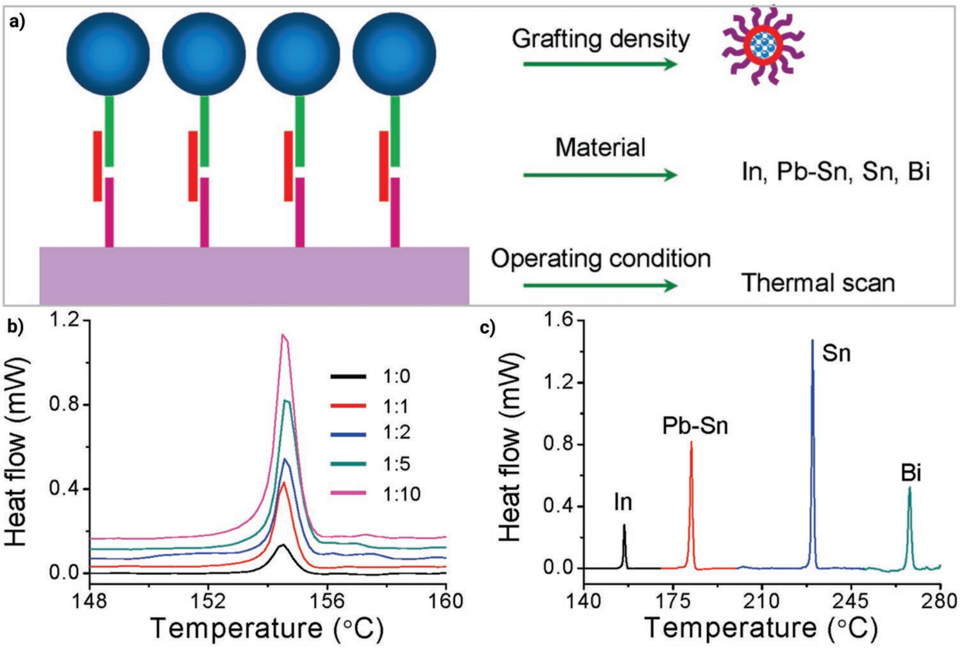

Figure 11. PCMs nanoparticles are used in biosensing. a) A ligand for the matching deoxyribonucleic acid (DNA) or protein biomarker is coupled to each kind of nanoparticle, which is subsequently immobilized on the ligand-modified substrate. The fusion enthalpies and melting temperature of nanosize particles reflect the kind and concentration of biomarkers, according to differential scanning calorimetry curve. b) The differential scanning calorimetry (DSC) curves demonstrate the influence of ligand grafting density on the range and detection sensitivity. c) The DSC curve exhibits the capacity to identify numerous compounds at the same time. Reproduced with permission.[94]

increase the shelf life of food goods, and maintain the cold chain during storage, transfer, delivery, and sale. PCMs have typically been employed in the food sector for heat storage and transit systems, for instance, heat processing sections, chilling storage, and packaging applications. PCM packaging is a cutting-edge solution for temperature-sensitive foods. PCM micro/nanoencapsulation is an effective way to enhance their performance.[99]

Researchers have used paraffin wax for LHS to store excess solar energy and release it when the energy availability is inadequate or not available. The impact of energy released from LHS was evaluated based on the drying kinetic energy of sweet potato. The results determined that the amount of energy extractable from the LHS was 1920 and 1386 kJ min kg^{-1} and the energy savings were 40% and 34% when using an inlet ambient

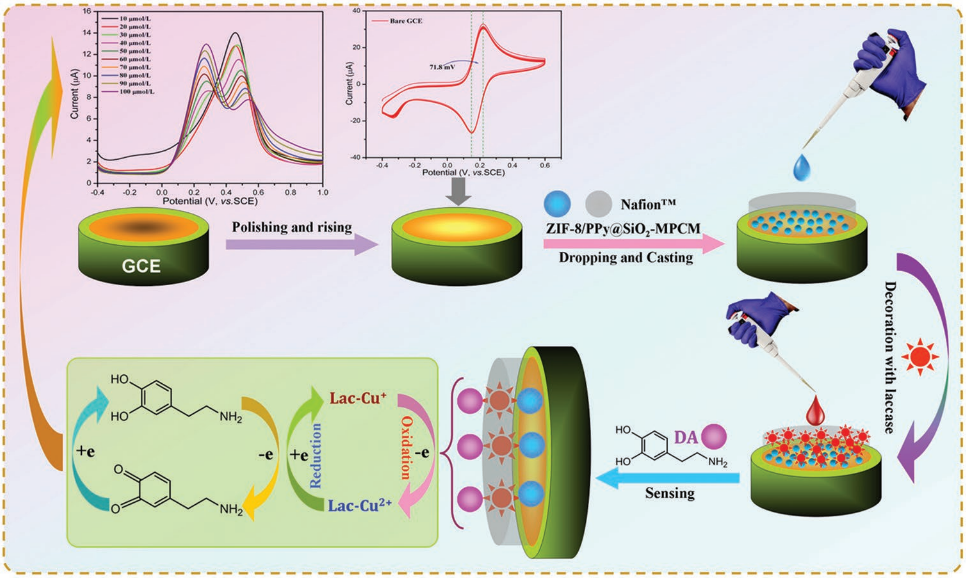

Figure 12. Illustrates the schematic development process of thermal self-regulatory biosensors for dopamine detection by incorporation of PCMs and metal-organic framework. Dopamine (DA), zeolite imidazolate framework-8 (ZIF), polypyrrole (PPY), silicon dioxide (SiO_2), glassy carbon electrode (GCE), laccase-copper (Lac-Cu^{2+}). Reproduced with permission.[95]

Table 6. Represents the applications of PCMs in food science.

Type of PCMs	Applications	Ref.
Paraffin waxes of Rubitherm	Chilly bins	[106]
Halloysite nanotubes/polyethylene glycol 400/600, polyethylene	Food packaging	[101]
Copper nanoparticles, interlocked polydivinylbenzene, microcapsules containing hexadecane	Food packaging	[107]
Paraffin waxes of Rubitherm	Food packaging	[108]
Dodecane	Smart food packaging	[109]
Climsel C18 and Cristopia E21	Food transportation system	[110]
Cristopia	Ice cream containers	[111]
Paraffin, and H_2O with 10% food-grade propylene glycol	Chilled food refrigerated cabinets	[112]
Paraffin wax	Drying of sweet potato	[100]
Deionized H_2O (98%) and borax (2%)	Food refrigerated cabinets	[113]
Octadecane and eicosane	Controlled release	[114]
Sodium polyacrylate, multiwalled carbon nanotubes, polyethylene	Vacuum insulation box for yogurt	[102]
Thermo-regulative phase change material (PCM) doped polyurethane (PU) foam	Perishable food cold storage	[105]
Diamine oxidase-immobilized electroactive phase-change microcapsules	Smart biosensor for detection of histamine in food	[115]

air velocity of 1 and 2 m s^{-1}.[100] In a study in 2021, polyethylene glycol (as a PMC) and halloysite nanotubes (aluminum silicate nanoparticles) were used as a thermal buffering agent in polyethylene to prepare nanocomposite film for flexible food packaging applications with significant potential to enhance food quality and food safety cold chain storage and transportation.[101]

In 2018, the cryogenic transport box was fabricated with sodium polyacrylate, multi-walled carbon nanotubes, polyethylene, and a vacuum insulation plate to store yogurt. The outcomes displayed that nanocomposites PCM can effectively maintain cold temperature for 87 h, and the pH and viscosity of yogurt remained at an acceptable level. Therefore, they claimed that their system ensures the quality of food, good cold insulation performance, and high feasibility.[102] In 2021, Rakshamuthu et al. reported zinc nitrate hexahydrate as a PCM in the solar dryer for gooseberries drying and preservation. The results displayed that the addition of PCM to the solar dryer enhanced the temperature and moisture removal rate compared to the conventional drying method.[103] Novel PCM-based packaging was developed using tetradecane to maintain and extend meat package quality and shelf life. According to the findings, the used PCM can maintain the meat packaging temperature at 12.5 °C uniformly for 133–137 min.[104] Sarkar et al., (2021) reviewed the developments in PCMS-doped energy-efficient polyurethane (PU) foam for perishable food-cold-storage applications for the temperature range between +15 to –10 °C. They tabulated suitable PCMs for cold storage applications and aimed to enhance the energy performance of perishable food cold storage. They concluded that the PCM's content and size, and encapsulation methods directly influence encapsulated PCM's properties and the energy performance of cold storage.[105] Different research on PCM applications in food sectors has been presented in **Table 6**.

The diamine oxidase-immobilized electroactive phase-change microcapsules were used in a smart biosensor to detect histamine in food at a low detection limit and high response sensitivity in a broad temperature range. The thermoregulatory smart biosensor enhanced the biosensing performance by thermal buffering at high temperatures (**Figure 13**). This is a new approach to creating high-performance electrochemical biosensors for the ultrasensitive detection of numerous dangerous compounds in foods under challenging environmental

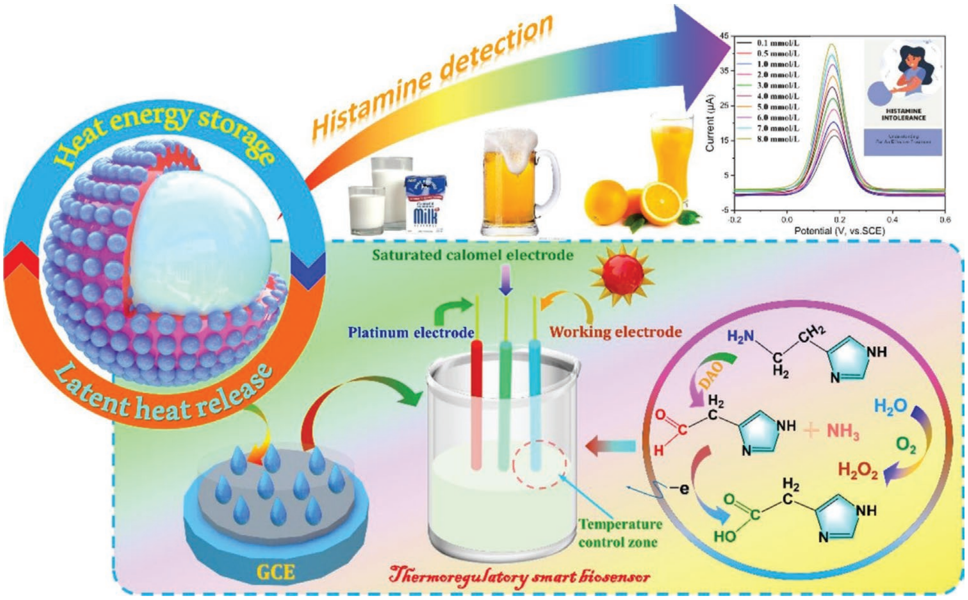

Figure 13. Illustrates the development of a histamine detector in foods at high-temperature environments using a phase change microcapsule. Glass carbon electrode (GCE). Reproduced with permission.[115] Copyright 2022, Elsevier.

circumstances.[115] In order to lessen the negative effects on the agricultural sector, individuals may now begin employing biological insecticides to eliminate and manage pests. The researchers enclosed Phermone (non-toxic and harmless biological pesticide) in hollow nano-cavity of halloysite nanotubes with rhythmical releases of *n*-octadecane under simulated diurnal temperature. The composite film exhibited a temperature on-off effect in the range of 15 and 30 °C. Besides, the outcomes demonstrated that the prepared film had an efficiently controlled release impact on myrcene and could adapt well to the circadian rhythm activity of some insects and can enhance the employment efficiency of insect pheromones.[116]

5.8. Additive Manufacturing

Materials and objects have benefitted from the advances in 3D printing technologies. 3D printing provides the ability to make an object with complex geometries and functionality and offers opportunities to incorporate active materials in the structure of 3D-printed objects.[117,118] Different dimensional nano additives have been studied, including 0D, 1D, 2D, and 3D nano additives and hybrid nanodevices.[119] Direct ink writing printing is one of the most used approaches because it is easy to use, has low cost, and has the potential to alter ink composition. The ink features should be highly viscose and shear thinning to hold their 3D printed shape after extrusion.[118,120] High-tech textiles use the benefit of 3D printing. Smart textiles use the PCMs for thermoregulation and the shape memory polymers that change the shape in response to the alteration in temperature. The role of 3D printing permits them to remove traditional design limits and design fascinating products.[121] 3D printing is a technique that can be used in life science applications and further study is required.

5.9. Applications of Artificial Intelligence (AI) and Machine Learning (ML) in TES of PCMS

Multiple disciplines (materials engineering, product and system integration, and device design) are researching thermal storage using PCMs. **Figure 14** represents the mechanisms, computational approaches, and experimental efforts, at different length scales within PMC thermal storage research and development. To create innovative materials, integrate PCMs with actual systems, and construct high-performance devices, it's crucial to understand the principles and interconnections of various length scales. Computational methods are developed according to these mechanisms and practical factors to optimize, design, and predict materials, systems, and devices. Experimental techniques give methods that permit manufacturing and prototype testing, evaluations of the property, and synthesis and characterization of materials.[10]

Lately, AI is increasingly acting as a key factor in monitoring, automation, intelligent recognition, management, information retrieval, and decision making. TES systems are able to become more rational and intelligent with the use of AI approaches, paving a new avenue for TES research.

The use of AI in TES can be classified into two main groups: optimization of TES design and operational control and modeling and prediction of TES performance. The application of AI in TES is illustrated in **Figure 15**. Research demonstrated that AI-based prediction models, such as the support vector machine and the artificial neural network, can accurately and rapidly predict TES performance and TES material attributes.[122] AI techniques are beneficial and promising in many aspects, for energy storage, including performance modeling, system control and operation, system design and evaluation, especially when external parameters have interfered or there are objectives such as cost and saving energy.[122] However, the current insufficiency of the TES database hinders the practice of AI-integrated TES. The characteristics of the future energy system should be reflected in AI-integrated TES research. ML and AI integrated with physics-based principles have the potential for design optimization and rapid performance prediction.[123]

Ren et al., (2022) employed ML approaches to forecast the actual time remaining to attain a pre-set melt fraction for PCMs during the melting process in real-time. They investigated an ML-based strategy on an artificial neuron network (ANN) for establishing efficacy and dependability for various forms of training data. They aimed to enhance the ANN model's predictability for estimating the time left to reach a predetermined

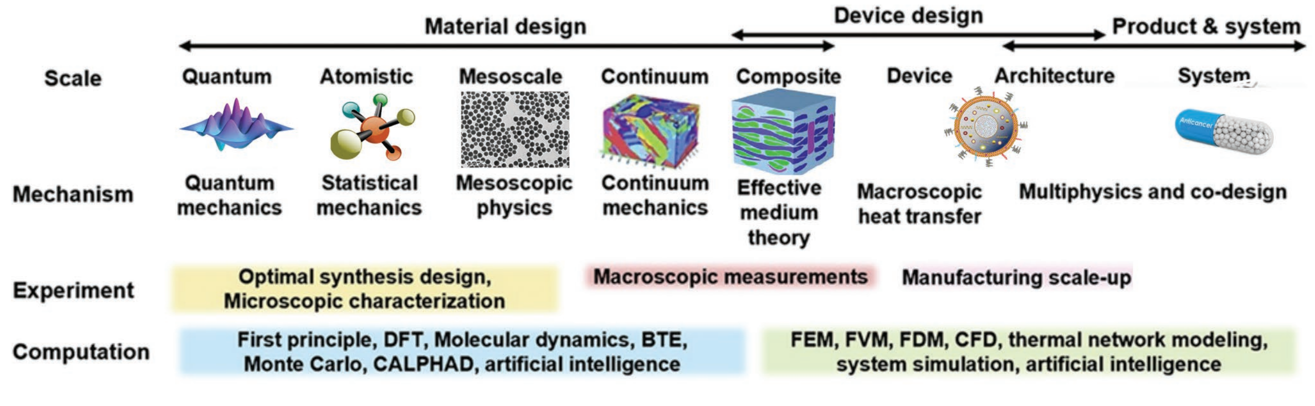

Figure 14. Illustrates length scales for PCMs in the devices, and systems, as well as modeling, design, and testing methodologies. FDM, finite difference method; CFD, computational fluid dynamics; BTE, Boltzmann transport equation; FVM, finite volume method; DFT, density functional theory; FEM, finite element method; CALPHAD, calculation of phase diagrams.

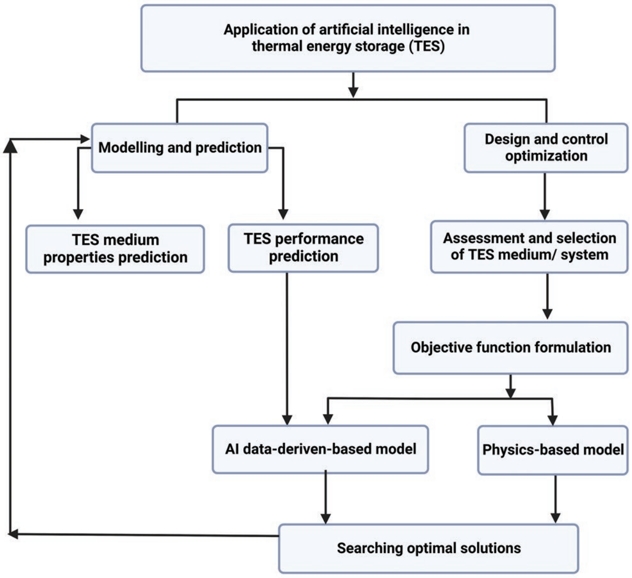

Figure 15. Schematic illustration of applications of artificial intelligence (AI) in thermal energy storage (TES).

melt fraction. The results showed that the developed ANN model was capable of forecasting with remarkable accuracy the time required to achieve a pre-defined melt-fraction value (e.g., 90% melt-fraction or 95% melt-fraction, as specified by the user). The mean error of the forecasts was computed and was projected to be less than 10 min, particularly during intervals of 30 min before the TES platform achieves the target melt fraction (i.e., 90% melt-fraction) over a total time span of 23 h.[124]

6. Challenges for LHS Systems

The following are the key issues that LHS faces in organic and inorganic PCMs. The PCMs applied to store latent heat are chosen based on several factors, such as non-toxicity, biocompatibility, reproducibility, high thermal stability, high latent enthalpy, relatively wide transition temperature range, and ease of chemical modification. Finding an appropriate material that meets all of the above requirements is the most difficult task. Even though PCM has a high TES density at a nearly constant temperature, it has significant challenges in practical TES applications. During phase transition, for instance, the volume change is considerable. Solid-liquid PCMs are widely employed because of their high latent heat of fusion and low volume expansion coefficient in comparison with other storage materials.[125] The positive aspect of eutectic PCMs than organic and inorganic PCMs is that they practically undergo any phase transition, solid-liquid or vice versa, consistently, and thus segregation possibility is lower.[126]

Incompatibility with plastic containers, low heat conductivity, and flammability are all drawbacks of paraffin PCMs. Flammability, instability at extremely high temperatures, poor thermal conductivity, and toxicity are the limitations of non-paraffin PCMs. FAs are mildly corrosive and are currently not cost-effective.[125]

The incongruent melting of most salt hydrates is a major challenge with inorganic PCMs. The solid salt separates and settles to the bottom of the container in a liquid state. When salt is frozen, it loses its ability to recombine with its hydration H_2O. It causes irreversible melting-freezing, and the essential heat storage materials (salt) deplete with each charge-discharge cycle. Apart from super-cooling and phase segregation, corrosion (particularly to mild steel), volume change during phase transition (which can surpass 10% in some situations), poor thermal conductivity near 1 W mK^{-1}, and lack of thermal stability are also significant issues with most salt hydrates.[125,127]

7. Conclusion and Future Perspectives

Recent progress clearly indicates the great potential of PCMs in life science applications. Among the different PCMs, organic ones (e.g., FAs and FA derivatives, polyalcohols and polyalcohol derivatives, PEG, and paraffin waxes) have the most promising properties. The main requirement to employ PCMs safely in life science includes biocompatibility and low toxicity. The PCMs are promising drug carriers for the treatment of life-threatening diseases. Most drug-related studies are focused on cancer treatment, which can be loaded and release various types of therapeutic agents. The challenges are to optimize the method for triggering the melting point of PCMs where needed, and the heat resistance capacity of the surrounding tissues. There are no commercial PCM materials for cancer treatments, although there are formulations in the early stage of clinical trials with a promising trajectory. PCMs have extensive applications in the medical dressing and textile industry as encapsulated materials or in fiber, to absorb and release heat based on the temperature of the body and environment, to prevent sweating and freezing. Medical dressings are an important kind of medical textile. A warm and comfortable environment is more conducive to wound healing, and it is very important to maintain a constant temperature at the wound. In packaging technology, PCMs have a significant role in preventing undesired warming and controlling the temperature of packaged food during storage and transport. PCMs can maintain package temperature by changing their phase, and by absorbing or releasing latent heat. For the commercialization of PCM in the packaging, further requirements are essential to be considered such as cost, regulatory aspects (labeling and multifunctionality), and consumer acceptance. Given the significant recent developments in the investigation of PCM for life science applications, for instance, drug delivery, food industry, biomedical science, etc. the authors are optimistic that PCM applications in life science will be commercialized in multiple sectors in the future. 3D printing of thermally responsive materials may open new possibilities for the development of PCM applications. In addition to the technical components, the environmental and social aspects of PCM-based TES are examined as part of the assessment criteria. Environmental characteristics and the cost of thermal storage systems are the key factors to link these techniques with actual applications. We hope that this review article will pique your curiosity in a field with vast potential in life science applications. PCMs will undoubtedly continue to be a source of technological and scientific advancement in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

life science applications, phase change materials, safety aspects, thermal energy assessment, thermal energy storage

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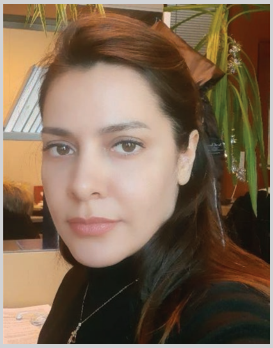

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