Review

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Review

Core/Shell Phase Change Materials: A Review on Green Synthesis and Their Application in Industrial and Energy Sector

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Abstract: Engineered substances that demonstrate superior properties compared with conventional materials are called advanced materials. Thermal energy storage systems based on Phase Change Materials (PCMs) offer an eco-friendly solution to reduce fuel and electricity consumption. The PCMs are compounds that can store thermal energy in the form of latent heat during phase transitions. Green synthesis of core/shell composite PCMs is an environmentally friendly method for producing these materials, focusing on reducing energy consumption, minimizing the use of harmful chemicals, and utilizing biodegradable or sustainable materials. Green synthesis methods typically involve natural materials, solvent-free techniques, green solvents, biomimetic approaches, and energy-efficient processes. This review presents the principles of latent heat thermal energy storage systems with PCMs in accordance with physical chemistry guidance. Furthermore, materials that can be used as PCMs, along with the most effective methods for improving their thermal performance, as well as various passive applications in the building sector, are highlighted. Finally, the focus on the combination of environmentally friendly processes and the performance benefits of composite PCMs that offer a sustainable solution for thermal energy storage and management is also discussed.

Keywords: phase change materials; green synthesis; core/shell material; energy efficiency; physical chemistry

1. Introduction

The Core/shell phase change materials (PCMs) are contemporary and innovative materials fabricated for effective thermal energy storage and release. They consist of a core based on a phase change material, such as fatty acids, paraffin, or inorganic salts encapsulated into a shell, which offers structural stability and reduces leakage during the phase change process.

In general, the synthesis and characterization of core/shell composite phase change materials (PCMs) include several considerations and key steps. Some synthesis methods include melt mixing [1], interfacial polymerization [2] and others such as evaporation of the solvent, coacervation, spray drying and layer-to-layer assembly which are microencapsulation techniques.

Many techniques can be used for the characterization of PCMs with respect to their morphology, structure, elemental composition, and thermal behavior. The most widely used physical chemistry methods for thermal analysis are the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and optical microscopy are used for structure and morphology characterization [3], Fourier Transformed infra-red (FTIR), ultra-visible (UV), X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopies are utilized for the analysis of chemical and structural composition and dynamic mechanical analysis (DMA) to test the mechanical properties [4]. The use of DSC aims to evaluate the thermal performance of the synthesized PCMs, assessing phase change temperature, crystallization and melting temperatures and latent heat [5]. The SEM was employed to visualise the

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morphology of the core/shell structure and ensure uniform encapsulation. FTIR characterisation was performed to confirm the chemical composition of the materials and to verify successful encapsulation.

Green synthesis of core/shell composite PCMs focuses on environmentally friendly methods where the energy consumption is reduced and the use of harmful chemicals is minimised to mitigate environmental damage and consequences. Its aim is to develop advanced materials that provide excellent thermal energy storage, durability and stability while reducing environmental impact. It has gained more attention because of its eco-friendly nature and alignment with sustainable development goals, but also, for its cost efficiency. By utilizing natural polymers, bio-based materials, renewable resources, non-toxic solvents or solvent-free processes, waste-minimizing techniques, researchers have pioneered more sustainable solutions for PCM production, enhancing their applicability in energy-efficient technologies and building materials.

The green synthesis of core/shell PCMs provides considerable advantages over traditional methods that align with sustainability principles. Several benefits are obtained by green synthesis, such as environmental friendliness owing to biodegradability and reduction in toxic chemicals, enhanced biocompatibility due to the presence of non-toxic shells, cost-effectiveness via the use of natural precursors and lower synthetic temperatures, and improved material properties that are assigned to the ability to synthesize well-defined core/shell structures with controlled morphology.

2. Synthesis and Characterization of Core/shell Composite Phase Change Materials

The green synthesis techniques aim to fabricate core/shell composite PCMs with minimal environmental impact. Therefore, the green synthesis emphasizes sustainable and energy-efficient methods to design and synthesize these composite materials taking into account the principles such as eco-friendly materials, green solvents, biomass-derived materials, emulsion polymerization, solvent-free techniques and natural/biobased extraction methods (Figure 1).

Figure 1. Principles of core/shell PCMs green synthesis.

2.1. Eco-friendly Materials

In the field of eco-friendly materials, renewable, biodegradable, or non-toxic materials for both core and shell components are utilized, such as natural waxes (e.g., carnauba wax, beeswax) and

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biopolymers (e.g., chitosan, alginate) [6]. Table 1 tabulates core/shell PCMs with respect to the green synthesis principles.

Table 1. Tabulated core/shell PCMs with respect to the green synthesis principles.

Core	Shell	Principle of green synthesis	Reference
Paraffin	TiO_2 -chitosan	Eco-friendly Materials	[7]
Lauric and stearic acid	PMMA	Eco-friendly Materials	[8]
1-dodecanol	Alginate, carboxymethyl cellulose and chitosan, Al_2O_3	Eco-friendly materials	[9]
Chia seed oil (fatty acids)	Whey protein, modified tapioca starch	Eco-friendly materials	[10]
Aluminium	Copper slag, bauxite	Eco-friendly materials	[11]
Paraffin	SiO_2 - PMMA	Green solvents	[12]
Crystal violet lactone, methyl stearate, bisphenol AF	Poly(urethane-urea)	Green solvents	[13]
n-octadecane	SiO_2	Green solvents	[14]
Paraffin - *Cocos nucifera* oil	industry generated tea waste	Biomass-derived Materials	[15]
n-octadecane	rice husk silica, rice husk carbon	Biomass-derived Materials	[1]
polyethylene glycol	carbon-based coconut shell	Biomass-derived Materials	[16]
Polyethylene glycol	Baboo flour	Biomass-derived Materials	[17]
N-Docosane	biomass waste lotus shells.	Biomass-derived Materials	[18]
1, 4-butanediol esters	Silica	Emulsion polymerization	[19]
1-dodecanol	Melamine-paraformaldehyde	Emulsion polymerization	[20]
Paraffin wax and n-octadecane	Melamine-formaldehyde	Emulsion polymerization	[21]
Cu-Si-Al	α-Al_2O_3 and AlOOH	Solvent-free techniques	[22]
Aluminium	$Cu(Mn_2O_4)/Cu(CrO_2)$, $FeMn(SiO_4)/Fe_2(SiO_4)$, and $Cr_{0.75}Fe_{1.25}O3$	Solvent-free techniques	[23]
Butyl stearate, hexadecane, caprylic acid	Pectin-barium chloride	Natural/ biobased extraction methods	[24]
Waste cooking fats	Biosilica, polypropylene	Natural/ biobased extraction methods	[25]
Avocado seed oil extraction	Biobased matrix	Natural/ biobased extraction methods	[26]

Chitosan is a natural cationic polysaccharide that is abundant and attractive to researchers for its bio-derivation, and thus was used for the synthesis of micro-PCM, for a shell that is TiO_2 -modified chitosan by Yu Song and his group. The goal of this study was to compose micro/macro-PCMs that are environmentally friendly, energy-storing, and thermally stable. Firstly, the micro-PCMs were synthesized with an oil-water-oil double emulsion and consisted of a paraffin core and the TiO_2 -chitosan shell. Another naturally derived material, alginate, was used as a matrix to form macro-PCMs and elevate the thermal stability and compression strength of the already UV- and temperature-resistant micro-PCMs. Alginate was incorporated into the PCMs using the piercing-solidifying method and $CaCl_2$. These micro/macro-PCMs are difunctional and propose an eco-friendly aspect to the core/shell PCM technology [7].

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As it was aforementioned, chitosan, an eco-friendly organic material with a plethora of functional groups, can be found in several studies as a shell material. Peng et al., used it to cover a polymethylmethacrylate (PMMA) shell and make bilayer shell core-shell PCMs, where the core consisted of lauric and stearic acid. The capsules were prepared using the microemulsion polymerization method, and a chitosan layer was added through electrostatic attraction. The nano encapsulated PCMs were then added to dressings. Through chemical structure and morphological characterization, it was found that they are dense and spherical structures. Additionally, this study shows that they have excellent thermal stability and the chitosan layer adds to their anti-leakage properties, their high-enthalpy preservation (in contrary to other shell materials that reduce the enthalpy of the PCM) and allows their application to more fields [8].

El Bouari et al., studied the encapsulation of PCM in different biopolymer shells for their incorporation into gypsum. The core was made of 1-dodecanol, whereas the biopolymers used were alginate, carboxymethyl cellulose (CMC), and chitosan. Each biopolymer was used to prepare the water phase, and nano-A_2O_3 was added to enhance the thermal conductivity of the materials. After the solubilization, 1-dodecanol in a molten state was added to form an oil in water emulsion. Reticulation solutions were used, different for each shell material, and subsequently, the PCMs were received in a gel form. After characterization, it was proved that the encapsulation of the 1-dodecanol core with biopolymers solved leakage and thermal conductivity problems. Specifically, the materials with chitosan and Al_2O_3 shells showed a higher compressive strength than those with other bio-shells. Phase change temperature was marked similar to that of non-encapsulated PCM with a decrease in latent heat. CMC and chitosan shells with Al_2O_3 maintained phase change temperatures, showing long-term stability and a decrease in enthalpies under both melting and freezing conditions. The CMC and Al_2O_3 shell was the one with the best thermal storage and stability properties, with possible use in building materials [9].

Kaur et al., used chia seed oil as the core and whey protein concentrate with modified tapioca starch as the shell for composite PCMs. Freeze-drying was used for the synthesis. The correct amount of each ingredient was selected to fabricate the optimum product with high encapsulation efficiency and high α-linoleic acid content. After the microcapsules were prepared, their fatty acid composition and thermal and oxidative stabilities were characterised. The results were promising since they showed stability in temperatures as high as 700°C and resistance in oxidation while, also, a higher content in Ω-3 fatty acids in contrary to Ω-6 ones. The last characteristic even makes them an interesting material for functional foods [10].

Copper slag is a byproduct of pyrometallurgy that poses a threat to the environment and is produced in large amounts. However, Zhang et al., used it to encapsulate commercial solid Al balls, making it eco-friendly. Using a two-step granulation method, a ceramic shell was placed on the core, which had an organic material on it, and sacrificed it to leave a cavity when the metal core melted. Copper slag replaced a part of the bauxite in the ceramic shell. Results showed improved heat transfer, thermal conductivity and sensible heat storage capacity, which can be attributed not only to the copper slag but also to the Fe_2O_3 formation on the outer layer of the shell [11].

2.2. Green Solvents

The category of green solvents includes environmentally benign solvents or solvent-free methods. For instance, a chemical waste reduction can be accomplished using water as a solvent or performing reactions under solvent-free conditions. Considering that water is a very easily accessible and common solvent, and is renewable and non-toxic, these properties enable it to be eco-friendly. Therefore, it is commonly used as a solvent in research studies. Li et al., explored the synthesis of core/shell phase change materials, where the shell was a hybrid of methyl methacrylate (MMA) and SiO_2. The method used for the fabrication was hydrolysis-polycondensation. For the experiment, the aqueous phase contained the surfactant sodium dodecyl benzene sulfonate and deionized water. After proper preparation, the oil phase, consisting of the monomer and silicon source, was added to the water phase. The remaining ingredients were added later, and hydrolysis and polymerisation occurred. The morphology, chemical composition, crystal structure, surface elements, particle size distribution, crystalline and thermal stability, and leakage were characterised. This green solvent process resulted in hybridized-shell/core microcapsules, with porous shells (structures with many cavities), great durability, energy storage and thermal conductivity. The products have possible applications as thermoregulation materials and even more because of their porous structure [12].

Water was also used as a solvent in a study by Liu and his group. The purpose of this study was to fabricate microcapsules that are reversible thermochromic and to apply them in anticounterfeiting. However, the products also showed phase-change properties and thermal stability, making the study notable. The synthesis of the core/shell phase change materials was performed via interfacial polymerization, avoiding the formaldehyde used in reversible thermochromic materials, owing to its harmful properties. The core contained crystal violet lactone as a color former, methyl stearate as a solvent and bisphenol AF as a developer, while the shell composition was poly(urethane-urea) (PUU) [13].

Ethanol is a widely used green solvent. In a study conducted by Siyi Ju et al., for the fabrication of core/shell PCMs as temperature-controlling materials, it was used as a solvent mixed with deionised water. More specifically, the synthesis was performed using the interfacial polycondensation method. The aqueous phase consisted of water, ethanol, and the surfactant, and was poured into the oil phase. After homogenisation and sonication, the mixture formed an emulsion. After the hydrolysis and polycondensation reactions, core/shell structures were formed in three different mass ratios. The capsules exhibited excellent thermal properties and strengths. A 2:1 mass ratio of the core to shell was added to the cement to test its compatibility. The results are very promising for the future of temperature cracks, since the addition of these capsules increased the capacity of thermal storage and of the hydration of the cement and can be applied to control the rise of temperature caused by the hydration of cement [14].

2.3. Biomass-Derived Materials

Several studies have been performed using materials derived from biomass, such as cellulose or starch, for the shell, that can provide biodegradability and mechanical strength [27]. The group of Phukan et al., synthesized a PCM using cocos nucifera oil and then formed stable PCMs using a tea waste matrix. The coconut oil was mixed with paraffin in five different ratios and consisted of a PCM. The mixture was then infused into the tea waste matrix, which was previously subjected to pyrolysis to form biochar via the direct impregnation method. The composite material was characterized and the results showed chemical and thermal stability and storage. The PCM 7:3 ratio of paraffin and coconut oil was found to be the one with the highest latent heat and impregnation effectiveness. Lastly, the thermal conductivity of the PCM was proved to be better than the bio composites containing each PCM alone [15].

Research performed by Chaoen Li et al., suggested the use of rice husks in phase change materials. Rice husk is a waste product abundant in China, where research has been conducted, and serves as a biomass material for the development of construction core-shell PCMs. This research explores two different applications in the fabrication of porous supporting matrices: rice husk silica and rice husk carbon. The method used to make the silica-based powder was the citrate treatment, while to make the carbon, pyrolysis in high temperature was applied. Subsequently, melted n-octadecane was added to two vacumised flasks, each containing one of the supporting matrices. The composite PCMs were ready after air was allowed in the flask and n-octadecane penetrated into the matrix. To prevent leakage, an epoxy resin was added to form a shell around the composite. These composite PCMs were synthesized at low cost and offer excellent thermal conductivity while being shape-stabilized and environmentally friendly [1].

Another approach in phase change materials supported by Kalidasan et al., used the shell of coconuts to synthesize, in a green two-step method. Coconut shell is an affordable solid waste that is agro-based, abundant in many countries like India where the research was done, that when carbonized is converted into biochar. Therefore, in this study, coconut shells were crushed, rinsed in

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deionized water, dried and then carbonized in 1000˚C in a tube furnace. Then their particle size was reduced and they were added to polyethylene glycol PCM to make the composites. For characterization, coconut shell nanoparticles were added in weight fractions ranging from 0.3% to 1.3%. The composites exhibited excellent thermal features because the energy storage potential increased during both heating and freezing. Optical absorbance was also increased and therefore, electromagnetic wave transmittance was reduced, with the 1.0% weight fraction enhancing the thermal conductivity a lot. These chemically stable composite PCMs containing coconut shell biochar are a sustainable proposition for future thermoregulation needs [16].

A bio-derived ingredient that has applications in the synthesis of PCMs is bamboo which is combined with polyethylene glycol (PEG). In this study, Xu et al., formed a phase-change material that was shape-stable through the vacuum adsorption method. First, bamboo flour was prepared by dry ball milling and then packed with PEG, with adsorption being better at longer milling times. The produced materials showed chemical, thermal and shape stability without any leakage and high encapsulation rate and thermal conductivity. The continuous bamboo fiber network structure was what improved these characteristics, compared to pure PEG. This research brings to light the benefits of bamboo utilization in phase change materials, without discarding the parenchyma cells, proposing the applications of the bamboo flour/PEG products for the composition of new composite materials with the potential of solar energy storage and incorporation in the building industry [17].

A PCM was produced in the research of He et al., derived from waste lotus shells. Firstly, the lotus was cleaned and then carbonized and activated. N-Docosane was incorporated into different surfaces via a vacuum impregnation method to form shape-stable phase-change composites. The materials were characterized and results showed that the materials with the activated lotus shell had excellent latent heat and thermal stability. These phase change materials are promising for utilization in thermal regulation for example in heat recovery and solar energy convention being sustainable and recycled [18].

2.4. Emulsion Polymerization

In the literature, natural surfactants have been widely used to stabilize emulsions, allowing for the encapsulation of the core material in a polymer shell. These surfactants are derived from sustainable sources that are eco-friendly, biodegradable, non-toxic and safe for human use. Several types of natural surfactants exist such as saponins derived from plants like yucca, soapwort, and quinoa; lecithin found in soybeans and egg yolks; sorbitan esters obtained from sorbitol, a sugar alcohol; rhamnolipids produced by bacteria; proteins and peptides found in milk or silk proteins; fatty acid derivatives derived from oils like palm, coconut, or castor; lipopeptides microbially produced.

In the work of Zhang Q. et al., for the synthesis of core/shell PCMs, an oil-water emulsion was created using Tween 80, a bio-based surfactant. The study followed the esterification of fatty acids with 1,4-butanediol using an iron chloride catalyst, the product of which was an ester core encapsulated in a silica shell. The encapsulation process was performed in a one-pot method by interfacial polycondensation, where an oil-water emulsion was formed. Two different samples were prepared with core/shell ratios of 1:1 and 2:1. The results showed regular spheres with good latent heat, thermal stability and properties like thermal management and regulation, with possible applications for overheating protection [19].

Another green method to synthesize core/shell PCMs is the use of no-surfactant techniques. Jitendra Singh and others took this approach in their study to make microcapsules of 1-dodecanol core and melamine-paraformaldehyde (MPF) shell. For the synthesis, the prepolymer was prepared in distilled water, and then PCM was added to the mixture. The prepolymer covered the PCM cores making micelles. The synthesis continued with the co-polymerization after the emulsion was formed. The same study followed the synthesis of these microcapsules using a Ramsden emulsion method with TiO_2 nanoparticles and compared them to a surfactant-free method. The results from the characterization of microcapsules from both methods showed that the second method is not only

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more environmentally friendly but it is, also, expected to be less expensive and difficult to prepare [20].

Zhang Zhe et al., used cellulose nanocrystals (CNC), which are natural and sustainable materials, as emulsifiers in a Pickering emulsion polymerization method. Paraffin wax and n-octadecane were used as PCMs. The method followed the addition of drops of a melamine-formaldehyde mixture in diluted CNC-PCM-stabilized emulsions. PCM microcapsules were obtained after in situ polymerization. The CNC not only acted as a surfactant but also as a reinforcing nanofiller in the shell. Overall, the PCM microcapsules exhibit excellent thermal properties at temperatures below 200 ℃. Furthermore, these materials are flame-retardant and thus, self-extinguishing and promising for many applications [21].

2.5. Solvent-Free Techniques

The production of core/shell PCM using solvent-free techniques not only reduces environmental hazards, but also simplifies the manufacturing process. Each method has specific operational requirements and material, making the choice dependent on the production scale, desired properties, and target application [28]. Several solvent-free techniques for producing core/shell PCMs can be used such as spray drying, melt dispersion, co-extrusion, electrostatic coating, fluidized bed coating, solid-state sintering, hot-melt encapsulation, in situ polymerization [28,29].

The study done by Masahiro Aoki et al., explored the synthesis of Cu-Si-Al core/shell phase change materials without solvents. The dry fabrication process is divided into two steps, the first is the High-speed Impact Blending (HIB) and the second is the heat oxidation treatment. Cu-Si-Al PCM particles were placed in a hybridization system with shell nanoparticles of α-Al_2O_3 and AlOOH to coat the PCMs. Then, in an oxygen atmosphere, heat oxidation occurred and the temperature went in 10 minutes from room temperature to 1000 °C and maintained there for three hours. Thus, the shell was stabilized. Three samples were prepared with different shells: one with alumina, one with AlOOH, and one with both. The characterization results showed optimal thermal stability and cyclic durability. Alumina and alumina-AlOOH shell PCMs with dual-layered shells exhibited the best thermal stability in high-temperature air. The incorporation of AlOOH enhances the thermal durability of the shell. This solvent free method is a cost efficient and green method that can be used in the synthesis of core/shell PCMs of different compositions [22].

Another novel synthesis of core–shell PCMs was conducted by Du and his co-workers. This study focuses on the synthesis of Al-based core-shell composites using a dry-mix extrusion method. In the cylindrical container, a core/shell structure was ensured between the spherical particles and the metal mixed-phase powder by using the centrifugal force of high-speed rotation. A sieving process was followed to ensure even heating and stable thermal properties, and then a calcination process was applied to reduce the deformation and decomposition risks. The composites were then added to the solar energy receivers which are analyzed below. The researchers investigated the environmental issues raised from this synthesis and noted the recyclability of the particles that is probable and needs further investigation [23].

2.6. Natural/Biobased Extraction Methods

These methods extract phase change materials from natural sources, ensuring that the process does not involve toxic solvents or harsh conditions [30]. The methods can be either bio-based PCM extraction that is used for plant oils and waxes, fatty acids [31]; or bio-derived shell material preparation that is used for chitosan, sodium alginate, cellulose [16]. The shell of the PCMs can be synthesized using bio-based polymers that are derived from renewable sources, reducing reliance on fossil fuels. Additional advantages of bio-based polymers are their customizability, biodegradability and the lower greenhouse gas emissions during production [6].

Chattopadhyay et al., investigated the use of pectin, a biodegradable, plant-derived biopolymer, to encapsulate organic phase change materials (PCMs) to enhance thermal energy storage. Using an ionic gelation method, pectin was cross-linked with barium chloride to form a shell around three

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types of PCMs: butyl stearate (an ester), hexadecane (paraffin), and caprylic acid (a fatty acid). The resulting pectin-PCM capsules, with a core content of 83-84 wt%, demonstrated notable thermal stability, sustaining temperatures higher than those of the unencapsulated PCMs. The functionality of each PCM, such as thermal buffering, varied based on its interaction with the pectin shell, with the peak encapsulation efficiency achieved through optimized core-to-shell ratios. The findings emphasize pectin's versatility and potential for sustainable PCM applications, particularly in temperature-sensitive storage solutions like packaging for perishable goods [24].

The investigation of Bragaglia et al., was based on sustainable PCMs, in which waste fat was extracted after cooking pork sausages. The fat was filtered through a strainer and allowed to cool. Characterization showed that the fat was mostly composed of saturated and unsaturated acids. To test its efficiency as phase change material, they integrated it into two different hosts, with the better one being the filter of a surgical face mask, and then they layered it on an exterior building wall. The thermal power that was transmitted with the layered PCM was reduced compared to that of the uncoated wall, proving the thermal energy storage capacity of the waste fat [25].

Avocado seed oil was extracted in a subsequent study to test its application as a PCM for the storage of cold thermal energy. Extraction was performed by steam drag, and the process began with the collected avocado seeds from food establishment waste being cleaned, washed, kept at low temperature, and ground. The product particles were then dried for 3 days, after which they underwent steam distillation. When the oil was extracted from this process, its phase change point was determined (for the solid-liquid transition). Results from tests on thermal boxes showed the oil's capacity of preserving cold temperatures and in some quantities proved it was better water [26].

3. Application Fields in Industrial and Energy Sector

Core–shell composite PCMs have a wide range of applications owing to their unique thermal properties and capability to deposit and release thermal energy. The versatility of core/shell composite PCMs enables them suitable for various applications, significantly improving energy efficiency and thermal management through various industries (Figure 2).

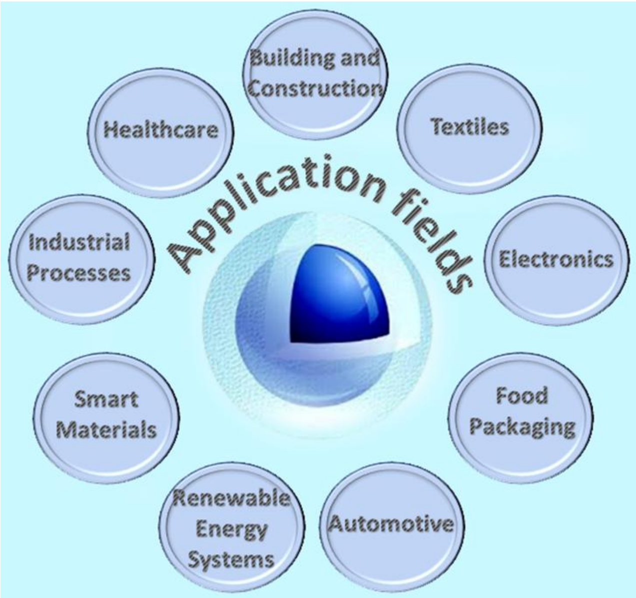

Figure 2. Application fields of core/shell PCMs.

3.1. Building and Construction

In the sector of building and construction, the core/shell PCMs are utilized in building materials to improve energy efficiency through the excess heat absorption during the day and the corresponding release during the night.[32]. An investigation the use of core/shell PCMs in cement

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slurries as a stabilizing agent of natural gas hydrate (NGH) layers in cementing in deep water. The core–shell PCMs contained low-binary PCM cores and $BaCO_3$ shells. They were synthesized via a self-assembly method and then integrated into cement slurries. The tests showed phase change temperatures of the microencapsulated PCMs that aligned with those of NGH formations (3.5˚C and 13.9˚C), reduced hydration heat generated by cement slurries, and more specifically reduced by 19% when the added PCM was at 9%, thus showing that the stability of the NGH is sustained. These PCMs proved to be great heat inhibitors, slowing heat release and at lower concentrations allowing the recrystallization of NGH back to a stable state [33].

The work of El Bouari et al., which explored different biopolymers as shells for a 1-dodecanol core, incorporated the materials in gypsum and tested them. Gypsum powder and the core/shell product with CMC and $Al2O_3$ shells were mixed and added to deionized water to form a homogenous composition. Different concentrations of the PCM were added, and the mixtures were left at room temperature to become solid and later evaluated. The results showed a small decrease in the compressive strength and thermal conductivity, while maintaining the mechanical strength above the minimum requirement. However, they also showed a controlled heat transfer rate during the heating and cooling procedures depending on the PCM amount in the matrix. This proves the usability of gypsum containing PCM for the improvement of the management of indoor temperatures [9].

Incorporating nano-enhanced, macro-encapsulated PCMs into cementitious composites has demonstrated significant thermal benefits in construction applications, particularly for cement-based mortars. Jong et al., achieved PCM encapsulation using an aluminum box-type macro-capsule, enhancing the strength, durability, and thermal conductivity, while effectively addressing leakage issues. Multi-walled carbon nanotubes (MWCNTs) were dispersed within the PCM, doubling their thermal conductivity and enabling improved energy storage and release at subzero temperatures. Cementitious mortars incorporating these nano-modified PCMs maintained internal temperatures above 0°C during thermal cycling, even when the ambient temperatures dropped to 5°C, highlighting their potential for energy-efficient thermal regulation in extreme climates. By stabilizing temperatures and reducing freeze-thaw damage, this composite approach could reduce heating costs and improve structural resilience in cold environments. Despite initial cost considerations, the enhanced performance and durability of the aluminum-encapsulated PCM system offer substantial long-term benefits for sustainable, energy-efficient construction in challenging conditions [34].

The application of core/shell phase change materials application in asphalt binders was tested in the work of Xue and his collaborators. Paraffin core and polymethyl acrylate shell PCMs were fabricated by in situ polymerization and incorporated into asphalt, where their effects were characterized. Overall, at high temperatures, the PCMs improved the response of the asphalt to temperature changes, thus preventing damage due to temperature increase. In addition, they improved viscosity and rutting resistance. Although, in low temperatures they were not effective and reduced storage stability and ductility, because of the different densities of the materials and the asphalt, these core/shell PCMs are a promising application in road construction for cooling pavements and propose further investigation [35].

Ardekane et al., synthesized copolymers of polyethylene/ polymethylmethacrylate (PEG/PMMA) and encapsulated the PCMs. Subsequently, the effect of the produced materials was evaluated in terms of energy conservation when applied to a building's facade. With the best PEG percentage of 60%, the composites were integrated via a simulation method on the surface of a sample building in six different cases. Annual results revealed that the PCM reduced both heating and cooling loads, with the first having a better decrease. Layer and location of the applied PCM plays a significant role in energy preservation, since incorporation of the PCM in external facades and northern and southern windows showed different results [36].

The work conducted by Yuan Gao and others explores the application of solid-solid phase change materials in windows for the purpose of solar radiation management and thermal energy storage. In this study, an equivalent to EnergyPlus's window was used as a simulator to investigate

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the energy savings of PCM windows. The s-s PCM used was based on poly(ethylene glycol). The inclusion of this semi-transparent material in translucent windows was tested in three different climates and showed excellent results. Solar absorption was the most efficient energy saving property in all climates. Thermal response was found to be dependent on many extrinsic factors, one of them being solar radiation heat. Overall s-s PCMs were proved beneficial for energy saving windows especially for the air-conditioning, ventilation and heating system, proposing more research for future building technology [37].

The next study of Kontoleon et al., investigated PCMs' incorporation in between glass and their effect on heat management and other parameters. Three organic phase change materials were tested in two different climates, facing different directions and in different states. Calculations were performed using a 3D model that resembled the real structure of a duplex building. Compared to conventional units that are double-glazed, PCMs offer high absorbance, low transmittance, and lower annual heat gain. Cost evaluation was the main objective of this research and the results showed a preference in the organic mixture 30 since it overall minimized heating and cooling costs in both climates and throughout the year, while it ensured ample daylight [38].

Fang et al., impregnated a bio-based PCM into an expanded glass aggregate (EGA) that was recycled, and the produced PCMs were covered with a fly ash shell. The PCMs had good thermal stability and were incorporated into cement mortar and managed to minimize the rate of heat transfer. They have proven to be useful for roofs and walls in buildings because they reduce the density of cement. Results, also showed lowered and delayed indoor peak temperature and good thermal properties and storage. From an economical aspect, long-term application of the materials is cost-efficient, and from an environmental aspect the materials are sustainable and have large scale application in a circular economy [39].

3.2. Textiles

The PCMs can be used to improve the thermoregulating properties of textiles. They can be incorporated into sportswear and apparel to maintain comfort by adapting to variations in body temperature. Moreover, they can be utilized in athletic clothing to manage the temperature and moisture during physical activity. Barani et al., examined this application while maintaining the integrity of the textiles. Cotton yarns were doped with core-shell nanocapsules with phase-change properties and then coated with polyacrylonitrile nanofibres. The PCMs used had a polymeric shell and n-octadecane core. To test the effects of doping, two different compositions were prepared and added to the yarn structures. PAN was added as a shell to form core-shell nanofibers to test its effect on the yarn. PCM was also added to the shell to investigate the effect of doping on the thermoregulation and tenacity of the cotton yarn. As for the results of the core/shell PCM application, they showed lower temperatures on the surfaces in hot environments, with the yarn that was doped both in the shell and core being the most cooling. They also showed a warming effect at cold temperatures. Overall, the PCM-doped yarn was more temperature-regulated during fluctuations in the temperature of the environment. PCM doping, also generally increased the tenacity values and decreased values of breaking elongation [40].

Li et al., investigated the synthesis and application of cross-linked and linear microencapsulated PCMs in textiles. Butyl stearate was used as the core, while the shell monomers were isophorone diisocyanate and triethanolamine for 2,4-toluene diisocyanate and diethylenetriamine, respectively. After fabrication, the materials were characterized, and their effect on the fabrics was examined. The cross-linked PCMs demonstrated better results overall, as their surfaces were dense and smooth, their wrapping effect was good, they did not show leakage, and their thermal stability was significantly better. The fabric that was finished with these PCMs had less yellowing after high temperature, showing the PCMs' low yellowing characteristics [41].

In the work of Guo et al., polyurethane/SiO_2-miniencapsuleted PCMs were prepared via an interfacial polymerization method using an electrostatic self-assembly technique. The core of the MEPCMs consisted of stearic acid butyl ester, while the shell was composed of polyurethane and

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SiO_2. SiO_2 was used to increase the thermal and chemical stability, thermal conductivity, and compactness and reduce the supercooling effect of the core/shell materials. After the cycling tests, the materials exhibited an optimal heat storage. These core/shell materials were then used to regulate the temperature of the textiles. The fabric samples were placed in a finishing solution made of PCMs and deionized water with an adhesive. Results of the coating were very promising on the temperature regulation [2].

Kumar et al., encapsulated 1-tetradecanol through in situ polymerization and then mixed it with an acrylic binder in three different ratios using three different techniques. After characterization, the material with the best durability, thermal properties, and add-on, which was the one with the 75:25 microcapsule-binder ratio, was used to coat the cotton fabric, and the results were examined. The mechanical properties of the fabric were not affected, with the exception of an increase in thickness and reduction in air permeability. Regarding the thermal properties, the thermal resistance was improved and the surface temperature was lowered. This research is another example of textile applications of PCMs that paves the way for textiles that are responsive to the climate, thermoregulated and sustainable [42].

Wang et al., encapsulated 1-dodecanol cores in a dual shell and incorporated them into a polyacrylate sheath. In this way, multi-core sheaths with a room-temperature phase-change point are fabricated. Fabrics containing these structures were tested and characterized. The results showed optimal mechanical properties, flexibility, and shape stability, whereas cycling tests did not affect their thermal reversibility and regulation. This study offers a novel incorporation of core/shell PCMs for the creation of smart textiles [43].

Li et al., designed and fabricated a series of reversible thermochromic MicroPCMs (RT-MPCMs) containing ternary thermochromic mixtures that were designed and fabricated via in situ polymerization. The RT-MPCMs exhibited stable light-to-thermal conversion ability, enhanced thermal storage capability, satisfactory thermal cyclic durability and thermal reliability. The state of energy storage or release can be monitored through color change, which is based on the phase transition properties of MeS. The smart adjustment-based garment demonstrated excellent intelligent thermo-regulated properties and used for keeping comfortable and constant body surface temperature due to the fact that it could absorb the latent thermal energy from the skin surface or environment heat [44].

Zhang et al., fabricated novel mixed-colorant thermochromic microcapsules (MCTMs) with conventional and thermochromic dyes as cores. The produced MPCMs exhibited enhanced reliability, encapsulation efficiency, and effective overheating protection. The obtained printed cotton fabrics, including MCTMs, can reversibly change colour between different tones with good durability and reliability, as confirmed by repeated cycles of isothermal cooling and heating processes. Moreover, more gorgeous colors were exhibited with respect to the common thermochromic materials [45].

3.3. Electronics

Core/shell composite PCMs can be used in power electronic devices for thermal management in order to dissipate heat and maintain optimal operating temperatures, to stabilize temperature fluctuations via the absorption of excess heat and then release it in demand when the operating system cools. Moreover, core/shell composite PCMs can be used in batteries and electric vehicles as well as in consumer electronics, providing uniform and enhanced heat distribution across devices.

Microencapsulated PCMs in the management of the temperature of satellite electronic boards were examined in a subsequent study by Mehrali and his collaborators. Lauric and stearic acids were used to form a eutectic core for the mPCMs. At an 82:18 molar ratio, the melting temperature of the mixture was 39 °C and was considered ideal for electronic boards according to the calculations. The shell was made of melamine and formaldehyde and the MF mixture encapsulated the core in an oil-in-water emulsion via in situ polymerization. Three different mPCMs were fabricated and characterized. The results showed that there was no chemical interaction between the core and the

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shell and that the encapsulation and latent heat improved as the core/shell mass ratio increased. The shell exhibited great anti-leakage properties, and the mPCMs showed chemical and thermal stability with a minor decrease in latent heat. The mPCM with the highest encapsulation ratio was used to control the temperature of the electronic board, and the results showed that at different constant electric power inputs, the heat sink with mPCMs reached the critical temperature with a significant delay. Furthermore, under pulsed electric power, the maximum temperature of the board decreased by 18 °C. Thus, this study proves the efficacy of mPCMs in controlling the electronic board's temperature [46].

Core–shell PCMs can also be applied in cold energy storage technology used in air-conditioning systems. The study of Cui Hongzhi et al., explored the encapsulation of salt hydrate PCM, specifically a type of PCM consisting of NH_4Cl, Na_2SO_4*$10H_2O$, and nanoclay, in different metals with higher conductivity than that of the PCM to improve the efficiency of cold storage. After corrosion tests on six metals, stainless steel and aluminum alloys were proven to be the most suitable for encapsulation. After corrosion, the products showed a reduction in thermophysical properties, while the effect of these properties on heat transfer was minor, with the aluminum alloy providing the best results. This study opens the way for the incorporation of metal-encapsulated salt hydrate PCMs in cold energy storage in air condition systems for bettering their durability and efficiency [47].

The work of Xiaoze Du et al., reports a dry mixing extrusion method to synthesize Al-based core/shell composite particles. Heat transfer/thermal energy storage materials were developed and were used as direct irradiation solid particle solar receivers. Their efficiency was enhanced, which was confirmed by the improved solar absorption, thermal storage properties, thermal stability, and mechanical strength. The obtained particles remain stable after elevated thermal treatment into violent collision environments [23].

The study of Xiaoze Du et al., introduced a sustainable, bio-based phase change material specifically designed for battery thermal management, addressing both environmental and performance needs. The researchers chose lauric and stearic acids to develop eutectic mixtures with optimal phase transition points suitable for battery temperatures. Ethylene-vinyl acetate (EVA) acted as a stabilizer, encapsulating the PCM to prevent leakage, while aluminum nitride (AlN) boosted thermal conductivity. To prepare the composite, fatty acids were blended and heated, with EVA and AlN added incrementally. An appropriate treatment of AlN was conducted to prevent hydrolysis and enhance thermal stability. The composite showed promising results, with a battery-compatible phase change temperature (37°C), significant heat capacity (107.94 J/g), and effective cooling, keeping battery temperatures below 45°C during high-discharge tests. This work offers an innovative solution for prolonging battery life and performance while minimizing ecological impact, marking a step forward in sustainable energy storage materials [48].

Other researchers have also addressed the use of microencapsulated PCMs for the thermal management of batteries. The work of Xiufang Ke et al., reports an organic-inorganic shell of MQ silicone resin for the encapsulation of the paraffin core via a precipitation method. At a 2:1 core-shell ratio, shape stability and thermal properties were the best. The microcapsules were then incorporated into a silicone rubber matrix to form a composite with improved mechanical properties. A 50 wt. % composite was tested for its thermal contribution to a prismatic $LiFePO_4$ battery. Results showed efficient thermal storage of the microcapsule since the applied composite controlled temperature within 5˚C, was able to lower by 10˚C the maximum temperature and the difference in temperature between parts of the battery [49].

The research of Wenbin Yang et al., introduced microencapsulated PCMs in a silicon rubber matrix to implement the material in lithium-ion batteries. However, the microcapsules were, also, reversible thermochromic. Microcapsules with a melamine formaldehyde shell and thermochromic core were synthesized via in situ polymerization and placed in a silicon rubber matrix. Subsequently, different amounts of Cu_2O were incorporated, and the composites were characterized. The presence of Cu_2O aided by making it possible the change in the color of the materials during the temperature changes and further improved the photothermal conversion and thermal conductivity. The

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application of flexible composites in lithium batteries was tested by introducing them to the battery heat. The obtained results showed reduced surface temperature of the batteries, proving the thermoregulation applications on batteries of these phase change materials that are flexible, multi-color and reversible thermochromic [50].

3.4. Food Packaging

The utilization of core/shell PCMs for food packaging presents several benefits such as the maintenance of optimum temperature, the improvement of thermal stability preventing degradation or leakage over time, the reduction of energy consumption because of the need for active refrigeration is minimized, the extended shelf life that is assigned to the spoilage prevention due to temperature fluctuations, and the sustainability because of the existence of biodegradable or recyclable shells [51].

In the work of Nafiseh Soltanizadeh et al., poly(ethylene glycol) that was used as a PCM was encapsulated into a shell based on alginate and $CaCl_2$ in three different concentrations. The packages containing the PCM appeared to be better at controlling temperature fluctuations, and furthermore, had a positive effect on other values, such as maintaining the pH. The results of this research show that the application of encapsulated PCM in fish packaging can be beneficial for its short time transportation without the need for freezers [52].

Another use of PCMs is their incorporation into the chocolate packaging. The group of Sujay Chattopadhyay et al., synthesized core/shell PCMs using an ionotropic gelation method and interfacial polymerization. The core consisted of beads that were 1-dodecanol embedded barium alginate, and the shell was made of polyurea, which provided anti-leakage and improved the thermal stability and flexibility. Encapsulated PCMs were used in chocolate packaging to test their effects. They are placed in the inner walls of a box that is temperature-controlled, and the goal is to maintain the temperature and taste of the chocolate for a longer time. The results showed a delay of 86.28 minutes in the change in steady temperature when the chocolate box was placed at approximately 35 ℃. Using encapsulated phase change beads can be beneficial for the maintenance of the chocolate's life and for the packaging of other foods during changes in the temperature of the environment [53].

In a study by Du et al., core/shell PCMs with a biodegradable shell were incorporated in meat packaging to control the temperature. Tetradecane was encapsulated in a calcium alginate shell, and after the capsules were characterised, they were integrated into the alginate films. The film with the highest concentration was selected for meat packaging. The results showed successful control of temperature rise, less changed physicochemical parameters and higher chewiness, gumminess, hardness and lower weight loss compared to samples not containing PCMs [23].

In the research of Saowapa Chaiwong et al., the PCMs' effect was tested on okra packaging. The materials were ice water bottles of commercial gel packs and were placed in two different thermal boxes and a foam box. After the temperature and quality tests, the foam boxes with or without PCMs resulted in CO_2 accumulation. However, thermal boxes with PCMs, especially with ice water bottles, showed reduced temperatures, maintenance of low temperatures, and reduced humidity, while the weight of the okra was almost unaffected. Therefore, PCM application in okra packaging was proved beneficial for cold chain management and for the improvement of the food's shelf life and maintenance of freshness [54].

3.5. Automotive

The ability of core/shell PCMs to efficiently manage temperature fluctuations and offer passive heating or cooling in vehicles enables them very useful in automotive climate control systems. According to these systems, comfort improvement can be accomplished together with a reduction in energy consumption. In the research of Srusti and Kumar, considering the passenger's best comfort, encapsulated PCMs with thermal melting points within thermal comfort temperatures were incorporated and tested in different positions and orientations in a car cabin. The effects of inorganic and organic PCMs were evaluated in this study. For the simulation, a new method called "equivalent specific heat method" was developed to reduce the computational time. Solar load distribution and

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its effect on temperature distribution, while, also, air temperature, phase change temperature and velocity contours were examined. Results were taken from 7 orientations and 16 locations in the car cabin and showed that two curvatures of inorganic PCM covering the roof best reduced the car cabin temperature [55].

In a systematic numerical study by Alhamany et al., with respect to battery thermal management, PCMs were incorporated in lithium batteries, contemporary with shape memory alloys, to improve the performance and safety of electric vehicles. PCMs were added as thermal regulation factors to extend the battery life and prevent excessive overheating. Combined with alloys, they provide thermal and mechanical stability, enhance storage, charging speed, durability, and reduce fatigue. It should be noted that the materials did not add to the weight of the battery and did not affect the design. Overall, this research suggests utilization of PCMs in electrical batteries for automotives, since they showed good results in improving autonomy, energy storage and thus safety, while it mentions the need for precautions during applications [56].

The research of Xiaoze Du et al., focused on PCM packages that were put in lithium-ion batteries. The goal of this study was to reduce the cost of battery thermal management systems and CO_2 emissions. The fabricated PCM module was flexible, high-capacity, and consisted of paraffin and thermally enhanced paraffin with nano-magnetite wrapped in a battery block. Testing under typical urban battery charge/discharge cycles and at different temperatures 30-40 ^{o}C demonstrated temperature stability at lower temperatures than conventional batteries. This way, battery life is increased and leads to a direct annual economic saving for medium electrical and hybrid vehicles, and, also, to lower CO_2 emissions depending with numbers depending on the fuel [23].

3.6. Renewable Energy Systems

Core/shell PCMs have remarkable potential in renewable energy systems, due to the fact that they pinpoint key challenges based on energy storage, energy efficiency, and temperature regulation. Their properties to provide thermal energy storage during periods of excess supply and then release it when there is a shortage enable them a significant solution in integrating renewable energy sources, such as wind, solar, hydropower and tidal (Figure 3).

Figure 3. Renewable energy systems.

Metal PCMs are useful in solar energy storage because they allow higher temperatures for concentrated solar power systems and improve the cycle efficiency of power generation. In a study by Pan et al., aluminium was used as PCM because it is compatible with concentrated solar power systems that operate above 565 °C owing to its melting temperature of 660 °C. The matrix used was expanded graphite and there was an oxidation pre-treatment to form a layer of oxide over the Al particles. This layer enhances the encapsulation and thermal properties of the PCM composites. In 1100 °C encapsulation reach the peak of 80 wt%, while between 600 and 700 °C the energy storage density was 248.5 J/g, making these composite PCMs preferable for the technology of high-temperature energy storage [57].

The study Hao Bai et al., explored core-shell nanocapsules with a stearic acid (SA) core and a silver (Ag) shell, created to enhance solar water heating systems (SWHS). Through a Pickering emulsion and reduction method, a high-conductivity Ag shell encapsulated SA, and thus boosted its thermal conductivity, significantly improving the system's thermal storage. Characterization results showed effective encapsulation, producing nanocapsules with diameters of 167–252 nm, which after suspensibility tests proved strong stability and suspensibility in water, which is crucial for consistent energy transfer in suspension systems. This core-shell structure suggests that these SA/Ag nanocapsules hold strong potential for more efficient, eco-friendly applications in solar energy storage [58].

The group of Farzan conducted a study to test the exergy and energy performance of a hybrid photovoltaic/solar air heater (PV/SAH) system. Encapsulated PCMs were employed to enhance electrical efficiency by reducing the PV temperature. PCMs were incorporated as a passive cooling method, absorbing heat and delaying its release, which cooled the PV cells and mitigated efficiency losses due to heat. However, the PCMs lowered the outlet temperature of the air heater, slightly reducing the thermal efficiency. In tests, PCMs reduced PV surface temperatures by up to 4°C, boosting electrical output by 6-7% while lowering daily thermal efficiency by 8-12%. This passive cooling boosted overall exergy efficiency, benefiting electrical performance despite a slight reduction in thermal output. It was, also, noted in the study that the size of the PV/SAH was bigger than the usual ones and this affected the results [59].

In another study by Sui et al., microencapsulated PCMs were incorporated into polyurethane (PU) to make a flexible photothermal film suitable for solar energy collection. Micro-PCMs were covered with polydopamine (PDA) and then mixed with PU at different weight ratios from 30% to 70 %. characterisation results showed that the film had a high photothermal storage energy because of PDA. PDA also improved the elongation of the films owing to its interaction with PU. The mPCMs-PU films demonstrated desired results in flexibility, photothermal cyclability, thermal durability and storage, proving to be ideal for use in thermal energy management and collection systems [60].

In a study by Ahmadi et al., a composite PCM of paraffin with a mixture of beef tallow and coconut oil was used on the surface of a photovoltaic (PV) module to increase heat removal. The PCM was a mix of different PCMs to combine their melting points into one material. Thus, they addressed problems such as uneven distribution, hot spots (high melting points), and limited time efficiency (low melting points). Weight effect measurements showed that the optimal ratio was 36.9% beef tallow/coconut oil and 63.1% paraffin [61].

As it was aforementioned, in the study of Xiaoze Du et al., Al-based core/shell PCMs were put under high temperature tests to evaluate their integration into solar thermal storage applications. After their dry mix extrusion synthesis, the tests conducted showed maintenance of solar absorptivity after days at high temperatures reaching 1200 °C with minimal mass loss and cost. Their compressive strength and energy density reached high values, proving their durability in applications in circulating flow. Their high thermal and solar storage and thermal conductivity makes them ideal for large scale solar thermal applications [23].

In a study conducted by Z. Al Hajaj and M Ziad Saghir, PCM (paraffin wax) was incorporated in a laboratory simulation of a geothermal energy pile system and was compared to a system that did not contain PCM. The application of PCMs in the system notably improved its thermal performance;

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it increased both the stored and extracted energy. Geothermal systems are a very useful source of energy for the heating and cooling of buildings and the PCM application in them could further improve heat exchange an storage capacity in future large-scale applications [62].

In a study by A. Torbatinejad et al., PCMs were incorporated in a simulation of geothermal energy sources, complementary to the addition of spiral fins to the exterior of the heat exchanger. Microencapsulated PCMs were placed in the backfill material. They were added in four volume fractions ranging from 0% to 50%. The results of this study showed that the temperature was reduced by 4 K with the use of PCM. Furthermore, the temperature difference in the backfill material became more moderate as the volume percentage increased. The best provided results showed efficiency of heat exchanger and coefficient of performance of the heat pump raise by 7.5%. in large scale applications, these results show promise in reduced energy consumption, cost and greenhouse emissions [63].

3.7. Healthcare

In literature several studies are based on the utilization of core/shell PCMs for healthcare applications such as temperature-controlled packaging that is used for transporting sensitive pharmaceuticals and medical supplies that require specific temperature conditions. Mohammed Taghi Zafarani-Moattar et al., focused on using bio-based PCMs for the nanoencapsulation of D3 vitamin, aiming at applications in thermosensitive drug delivery. Researchers selected a eutectic mixture of stearic and lauric acids (1:3 mole ratio) with a phase change temperature close to body temperature (35.6°C), ideal for controlled release. Vitamin D3 was encapsulated in this PCM using stabilizers like polyvinyl alcohol and polyvinylpyrrolidone, along with sodium lauryl sulfate as an emulsifier. Characterization showed high encapsulation efficiency and stable core-shell nanocapsules with smooth morphology. The 35:65 shell-to-core weight ratio was confirmed, while quick, temperature-responsive vitamin D3 release was demonstrated in release studies at 37°C, highlighting this PCM’s potential for delivering sensitive drugs within body temperature ranges [64].

Eutectic mixture PCMs were encapsulated together with Rhodamine B, a model drug, in ethyl cellulose nanofibers via blend electrospinning in the work of Ping Lu and his collaborators. The goal of this study was to achieve temperature-sensitive drug release in the human body, particularly for antibiotics, anti-inflammatory drugs, and chemotherapy. The PCM loading manipulation led to tunable release rate of the drug, with 5 and 10% showing steady release and 20 and 40% showing burst release at 37 °C. The obtained results are very promising for the future of temperature-responsive drug release.[65].

The work of Shujun Wang et al., reported the fabrication of natural core–shell sporopollenin microcapsules to control lipid absorption in obesity. Naturally occurring micro/NPs provide an incredible array of potential sources for fabricating pharmaceutical microcapsule carriers. Natural pine pollen was treated with phosphoric acid to yield intact, clean, and monodisperse microcapsules. The intrinsic core–shell structures of natural pine pollen have been used as potential carriers for pharmaceutical microcapsules owing to their excellent liquid absorption abilities and tunable wetting properties. It was proved that the aforementioned hydrophobic sporopollenin microcapsules, are able to selectively adsorb oils in water–oil systems within the organism [66].

3.8. Industrial Processes

Several industries operate process heat management as an application to regulate temperatures for energy efficiency improvement during procedures that generate excess heat (Figure 4).

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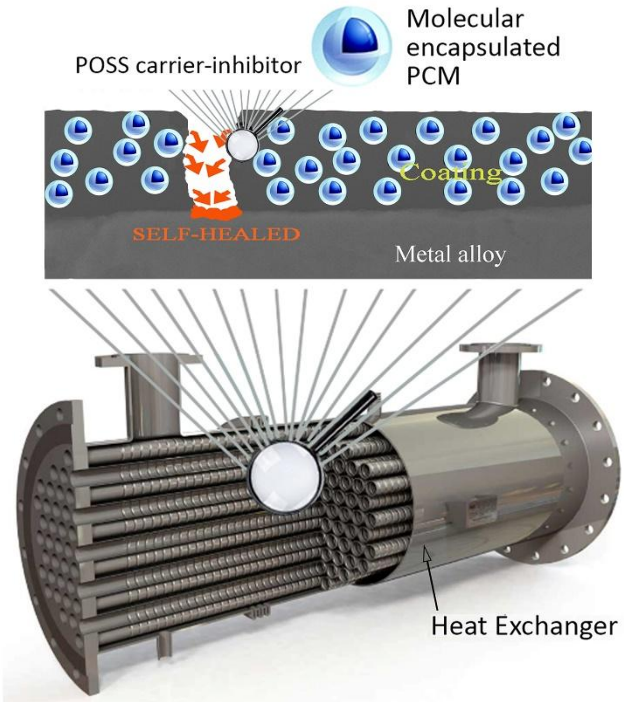

Figure 4. Industrial processes using heat exchangers (PCMs).

The research of Changgui Xie and Xiao Yang explores the effect of nano-encapsulated phase change materials in microchannels for the bettering of thermal management of fuel cells. More specifically, PCMs consisting of a PMMA shell and an n-octadecane or salt hydrate core were employed in a molten state to test the influence of changes in the Reynolds number, their volume fractions, and the temperature of the bottom plate of the aluminum cast on the absorption of heat. The microchannel used was an aluminum cast structure with tubular hollows to allow the flow of a water-PCM mixture. The tests of the research led to results that proposed numbers for improving microchannel heat transfer systems with applications, especially in fuel cells. With the improvement of their thermal management maintenance of the cell's performance, prevention of thermal degradation and uniform distribution of temperature within the cell will also be enhanced [67].

In a study by Peng Zhang et al., PCMs were placed on shelves of an apple refrigerator warehouse simulator to test their effectiveness in low-temperature storage. This study investigated the performance of PCMs in postponing the alleviation of electricity requirements and economic, thermal regulation, and preservation. Results showed that PCMs can help reduce the cost of operation of the warehouse, the peak air temperature by 1.1 degrees Celsius and maximum temperature rise rate of the apples in comparison to a warehouse without on-shelf PCMs. While there are some defects like slightly increased temperature in the last 6 hours of storage in one day, the on-shelf PCM incorporation in food warehouses shows promise for future energy and food preservation [68].

The work of Shohel Mahmud et al., deals with PCMs that are used in a food storage refrigerator combined with solar energy and thermoelectric cooling. The PCMs' goal was to maintain the refrigerator temperature at 5 °C. Fruits and vegetables with moisture levels of 50–99% were selected for testing. The results showed that the average time of solidification of the PCM was approximately 3.5h and the coefficient performance was 0.69. The water flow through copper pipes for thermoelectric cooling was also proven to be beneficial and even reduced the solidification time of the PCM by one hour. Future research is needed for the optimization of results and for applications in large scale [69].

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3.9. Smart Materials

Smart buildings demonstrate enhanced energy efficiency due to the fact that include materials that respond to environmental changes. In a study by Li et al., core/shell thermochromic phase change materials were integrated into wood to induce a phase change in the next study. Microcapsules with a melamine-formaldehyde shell and an ethyl stearate, methyl stearate, and crystal violet lactone core were synthesised and then mixed with polyvinyl alcohol to form a thermochromic solution. The mixture was added to Hinoki wood, forming a coat over it, using the drop-coating method. This new material is now a composite with thermal energy storage and reversible thermochromic properties. Characterization results showed that thermochromic phase change wood had thermal stability in the temperature range of 26-270˚C, with phase change temperature of 34 degrees Celsius, around human body temperature. This fact makes it applicable to places like home décor and other human places because it makes it low toxicity and environmentally friendly. This composite material, also, responded to thermal changes changing colors; with an increase from 34˚C it changes from a bluish color to yellow. Its thermal storage and thermochromic properties make it a promising material for smart home systems, the functional material industry and a sustainable future [70].

The group of Jianwei Zhang et al., investigated the production of core/shell capsules with a core derived from waste cooking oil where integrated into asphalt to delay their rate of changing temperature and therefore prevent damage of asphalt pavements in the hot weather. Waste cooking oil was used to extract from it its waxy components. These components (methyl palmitate) underwent hydrolysis to have a phase change temperature and enthalpy closer to that of asphalt (palmitic acid). The phase change materials were made via the orifice coagulation method. The shell consisted of cross-linked calcium alginate. The ratio was 1:1 making the capsules thermally and mechanically stable with optimal thermal energy storage [71].

A core derived from cooking oil was, also, used in the study of Fan Yansong et al., to improve thermal response of walls in buildings. Microencapsulated PCMs, were synthesized this time via the suspension polymerization method and methyl palmitate itself was incorporated. The shell was methyltriethoxysilane to prevent leakage. The microcapsules were put in foamed cement and characterization results showed improved compressive strength and suitability for the cement's thermoregulation. While they need to more researched, these materials open the way for recycled materials to aid in energy consumption and make smart building materials [72].

The work of Michele Bottarelli et al., explores the fabrication of a PCM for heating and one for cooling were put into radiant floor in a large-scale investigation to test how it stores and releases thermal energy and how it controls heat gains throughout the year. The PCMs were macroencapsulated hydrated salts and they put in a checkerboard pattern in a snack-bar space with an air handling unit that managed latent loads and ensured rates of ventilation. They had different melting temperatures, 27 and 17 degrees Celsius for summer and winter. Effective storage of thermal energy was noted, since both during the summer and the winter, PCM absorbed and released heat, maintaining temperature and saving energy by limiting the need of the air handling unit [73].

4. Challenges

Principally, core/shell composite PCMs provide significant advantages for thermal energy storage and management, but it may be remarked that several challenges are also faced [74]. Taking into consideration challenges based on encapsulation efficiency, thermal stability, cost of materials, scale-up issues, compatibility, heat transfer efficiency, environmental concerns, core/shell composite PCMs can become more effective and widely used in various applications.

Achieving High encapsulation efficiency achievement without compromising the shell structural integrity can be difficult. Poor encapsulation may lead to leakage of the core material. To avoid this, a study, firstly puts an oxide shell as an oxidation pre-treatment. According to this way the encapsulation ratio was increased, and leakage was prevented [57]. A double shell is another solution to leakage problems. Chitosan is used as the second shell to prevent leakage [8]. A very

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crucial factor is the thermal stability of the shell material. Several polymers can be degraded at elevated temperatures, which may limit the operational range of the PCM. An action taken to enhance the thermal stability, for example in this research [24] and the biopolymer was crosslinked with barium, alumina and alumina-AlOOH shells showed the best thermal stability [22].

The shells of biopolymers or advanced materials can be more expensive than conventional materials, which may prevent their large-scale commercial adoption. Balancing affordability with performance is a persistent challenge for manufacturers. However, economical production methods use waste byproducts.

Scaling up the synthesis process from laboratory to industrial levels can be challenging, particularly in maintaining the quality and uniformity of the core/shell structure. Most research has been conducted in laboratories with simulations [68], refrigerator simulation [38], 3D model of building [63] simulation of geothermal sources, etc. Continuing to large-scale production, issues such as uneven particle size distribution and agglomeration may arise, and different techniques may be needed during the synthesis. Additionally, reactor designs may require optimisation of emulsification or polymerisation processes.

A very important factor is that the shell and core materials have to be chemically compatible in order to avoid reactions that could influence performance or stability. For instance, hydrophobic and hydrophilic mismatches can lead to phase separation or ineffective encapsulation. Compatibility challenges are also observed when conductive fillers are added because of their potential to alter the properties of the shell.

Considering the heat transfer efficiency, it may be noted that while PCMs effectively store energy, their heat transfer rates can be slow. Enhancing thermal conductivity is essential for improving performance. This disadvantage can be overcome by using modified material in the shell or using shell materials that themselves have high thermal conductivity [74]**.** For example, alumina helped accelerate the heat transfer efficiency **[22].** Another metal oxide that can be used in the shell to enhance the thermal conductivity is SiO_2. Although many PCMs are designed to be eco-friendly, the fabrication procedures and end-of-life disposal of some materials still cause environmental concerns. The biodegradability and recyclability of the PCMs that are produced require further investigation; therefore, after use and wear of the products, they can be revived, reused, or disposed in an environmental way.

5. Summary and Outlook

This review reports the green synthesis of core/shell PCMs, emphasizing environmentally friendly methods of design, production and application. Traditional synthesis procedures for PCMs usually involve the utilization of toxic chemicals and energy-consumption processes. On the other hand, green synthesis, aims to minimize environmental impacts through the use of non-toxic solvents, renewable resources, and low-energy methods. This approach reinforces sustainable development and maintains the main functional performance of the PCMs.

Future directions for core/shell composite PCMs are promising and focus on enhancing sustainability, performance, and applicability across different sectors. Studies on new, sustainable materials for both shell and core components, such as bio-based polymers or nanomaterials, can improve performance and minimize environmental impact. The development of innovative synthesis methods, such as additive manufacturing or self-assembly techniques, can allow for more accurate control of structure and properties. The incorporation of conductive additives such as conductive polymers, carbon nanotubes and graphene into the PCM matrix can enhance the thermal conductivity without affecting encapsulation. Moreover, investigations based on PCMs that can provide additional functionalities such as antibacterial properties, fire resistance, and moisture control could result in a wide range of applications. In an already mentioned study the core/shell materials were not only PCMs but also thermochromic compounds providing the produced wood with the same properties [70]**.** Finally, comprehensive life cycle assessments should be conducted in

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a direction of better understanding the environmental impacts of PCMs with the ultimate scope of their sustainability improvement.

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Abbreviations

The following abbreviations are used in this manuscript:

PCMs	Phase Change Materials
AlN	Aluminum nitride
CMC	Carboxymethyl cellulose
DMA	Dynamic mechanical analysis ()
DSC	Differential scanning calorimetry
EGA	Expanded glass aggregate
EVA	Ethylene-vinyl acetate
FTIR	Fourier Transformed infra-red
HIB	High-speed Impact Blending
MCTMs	Mixed-colorant thermochromic microcapsules
MMA	Methyl methacrylate
MPF	Melamine-paraformaldehyde
MWCNTs	Multi-walled carbon nanotubes
NGH	Natural gas hydrate
NMR	Nuclear magnetic resonance
PDA	Polydopamine
PEG	Polyethylene glycol
PMMA	Polymethylmethacrylate
PU	Polyurethane
PUU	Poly(urethane-urea)
PV	Photovoltaic
RT-MPCMs	Reversible thermochromic MicroPCMs
SA	Stearic acid
SAH	Solar air heater
SEM	Scanning electron microscopy
SWHS	Solar water heating systems
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV	Ultra-visible
XRD	X-ray diffraction

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