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Advanced Energy Storage Solutions: Innovative Approaches to Microencapsulation of Phase Change Materials

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Abstract

Phase change materials (PCMs) represent a significant innovation in thermal energy storage systems, enabling the controlled absorption and release of energy as needed by a system. PCMs find extensive application across various domains, including but not limited to buildings, textiles, electronic devices, and heat management for batteries. These materials are favored for their remarkable qualities, such as high energy storage density, cost-effectiveness, reusability, minimal interference with the system, and adaptability to a wide range of temperatures. However, the application of PCMs often encounters challenges related to leakage when exposed to different environments. Microencapsulation emerges as a viable technique to safeguard PCMs against external factors and leakage issues, while preserving their thermal energy storage capabilities. Over time, numerous physical and chemical methods have been developed to produce microcapsules with robust mechanical integrity and long-term stability. Nonetheless, none of these methods can deliver Microencapsulated Phase Change Materials (MEPCMs) with all the desired properties. To fully harness the potential of MEPCMs, there is a need for innovative techniques that enhance their structural stability and extend their service life. Existing approaches may require modifications, such as the incorporation of nanoparticles and binding materials, to improve their overall performance. This paper offers an overview of PCM types and shell materials used for encapsulation, common microencapsulation methods, and the characterization techniques employed to assess the properties of developed MEPCMs. Furthermore, the paper delves into the limitations and advancements in this field, shedding light on the evolving landscape of PCM encapsulation technology.

Keywords: Microencapsulation, Phase change materials, thermal energy storage, properties

1. Introduction

Phase Change Materials (PCMs) represent one of the most prevalent energy storage systems, where processes like melting, sublimation, and vaporization absorb heat from the surroundings, while solidification or condensation release heat into the system when required. Encapsulation has emerged as a widely employed technique for large-scale PCM applications, as it provides notable benefits such as increased heat transfer area, reduced corrosion, control of volume change during phase transitions, and improved compatibility with the surrounding environment. Depending on the size of the capsules produced, encapsulation is categorized into three classes: Macroencapsulation (1 mm to 1 cm), Microencapsulation (1 µm to 1 mm), and Nanoencapsulation (< 1 µm). Among these, microencapsulation is the most commonly employed method due to its superior stability and ease of preparation when compared to nanoencapsulation. PCMs find applications in a variety of fields, including buildings, textiles, food packaging, and heating and cooling systems. The incorporation of Microencapsulated Phase Change Materials (MEPCMs) into textiles and building materials enhances thermal mass for energy storage without significantly increasing the overall mass of the structure. PCMs are currently being used in absorption refrigeration, air conditioning, and cold energy storage systems for cooling applications in buildings. Microencapsulated Phase Change Material Slurries (MPCS) have also gained prominence, as they involve encapsulated PCMs blended with a carrier fluid, serving as a secondary refrigerant in cooling applications. This innovative approach contributes to increased energy efficiency and reduces the demand for traditional refrigerants, aligning with the imperative for sustainable and environmentally friendly energy practices [1].

2. Phase Change Materials (PCM)

Phase Change Materials (PCMs) represent the predominant choice among Thermal Energy Storage (TES) systems, effectively absorbing and subsequently releasing energy as needed. Their versatility in storing both latent and sensible heat makes them an ideal component for energy storage. The total heat content stored can be quantified using the formula established by Raj and Goswami (2018, [2]):

$$Q = m\left[\left\{\int_{T_s}^{T_m} C_{ps}dt\right\} + \Delta h_m + \left\{\left\{\int_{T_m}^{T_i} C_{pl}dt\right\}\right\}\right]$$

(1)

Phase transitions in PCMs typically occur in response to pressure, strain, light, or heat stimuli and manifest in four distinct forms: Solid-Liquid, Solid-Solid, Solid-Gas, and Liquid-Gas. Solid-solid transitions involve minimal volume changes and do not necessitate encapsulation techniques but are characterized by lower heat transfer efficiency. During these transitions, PCMs may undergo structural changes, such as lattice configuration conversions, with minimal physical alterations, leakage, or supercooling. In the context of building applications, PCMs exhibiting significant volume changes, such as Solid-Gas and Liquid-Gas transitions, are unsuitable as they may compromise the structural integrity of buildings. Additionally, these PCMs may generate high internal pressure, affecting the mechanical stability of the application [3].

PCMs undergoing Solid-Liquid and Solid-Gas transitions are challenging to handle without protective encapsulation, as they may leak into the surrounding system. Ideal PCM characteristics can be categorized into three main requirements: physical, chemical, and economic. The physical prerequisites for a suitable PCM encompass high thermal conductivity (K), a high specific heat capacity (C_p), phase change temperatures within the desired range with minimal supercooling, complete reversibility of the melt/freeze cycle, favorable phase equilibrium, low vapor pressure during operation, and a sufficient rate of crystallization. Key chemical requisites include excellent physical and chemical stability over repeated cycles, low vapor pressure, absence of supercooling and sub-cooling, flame resistance, non-hazardous properties, absence of explosive compounds, corrosion resistance when encapsulated, high compatibility with surrounding materials, and non-incongruent melting. From an economic perspective, ideal PCMs should be abundant, cost-effective, reusable, and recyclable [4].

The functionality of PCMs revolves around heat exchange, wherein they absorb and store latent heat energy from the system, subsequently releasing it to the environment during crystallization or reverse cooling [5]. Temperature fluctuations in PCMs during crystallization and melting stages are minimal. The chemical bonds within the PCM material break as they absorb heat from the system during temperature increases, and these bonds are restored during the crystallization process, releasing the absorbed energy [6].

Various methods exist for integrating PCMs into applications, including encapsulation, shape-stabilization, immersion, and direct incorporation. Encapsulation entails containing the PCM within a suitable shell material, while shape stabilization embeds the PCM onto a compatible supporting material. Immersion and direct incorporation methods are more prone to leakage issues.

3. Classification of PCM

PCMs can be generally classified into three broad categories: inorganic, organic and eutectics.

3.1. Inorganic

Inorganic Phase Change Materials (PCMs) are popular alternatives to organic PCMs, offering several key advantages, such as high thermal conductivity, substantial phase change enthalpy, small volume change during phase transition, cost-effectiveness, non-flammability, recyclability, and a high latent heat capacity. However, they do present challenges, including potential corrosiveness to metals, supercooling, phase segregation, toxicity, decomposition, incompatibility with construction materials, dehydration, incongruent melting, limited nucleation ability, and a relatively narrow temperature range of application [7].

3.1.1. Salt Hydrates: Among inorganic PCMs, salt hydrates stand out as an economical option. They are readily available as by-products from various industrial processes, with minimal volume changes (less than 1%) during phase transition. While they exhibit high density (around 1640 kg/m^3), their heat of fusion can reach up to 296 kJ/kg, and they boast a thermal conductivity of 0.6 W/mK, making them suitable for a wide range of applications. Salt hydrates typically have a transition temperature range of 25-34°C, making them particularly useful in comfort cooling applications. Challenges with salt hydrates include incongruent melting and supercooling, but they demonstrate mechanical and thermal stability during repeated cycling. Techniques like altering chemical composition, mechanical stirring, and introducing nucleating and thickening agents helps to mitigate these issues. While salt hydrates exhibit slightly lower thermal conductivity and a less degree of toxicity, they remain a practical choice. Commonly used salt hydrates include Lithium metaborate octahydrate, Magnesium nitrate hexahydrate, Calcium chloride hexahydrate, and others [8].

3.1.2. Low Melting Point Metals: Low melting point metals and alloys, known for their high thermal conductivity and heat transfer capabilities, are valued for their exceptional heat storage capacity per unit volume due to their inherent high density. Their benefits include non-flammability, minimal volume change during phase transition, high boiling points (>2000°C), reduced vapor pressure, and high latent heat values due to strong intermolecular bonding. However, cost considerations, as well as their elevated thermal and electrical conductivities, which can lead to rapid energy release, can pose challenges. Corrosion with the surrounding environment is another concern. Common low melting point metals include Rubidium, Gallium, and Caesium, while eutectic alloys like Lead, Cadmium, Indium, Bismuth, and Tin are also utilized. These metals find applications in cooling systems for devices such as smartphones, USB flash drives, and laser systems [9].

3.2. Organic

Organic PCMs have gained widespread recognition in contemporary applications. Their notable advantages include corrosion resistance, low toxicity, good compatibility with building materials, minimal volume changes, reduced issues like super-cooling and phase segregation, and excellent thermal and chemical stability with high thermal energy storage capacity. However, drawbacks include low thermal conductivity, low enthalpy of phase change, volatility, flammability upon heating, higher cost compared to inorganic PCMs, and significant volume changes, especially in the case of paraffin compounds [10].

3.2.1. Paraffin Waxes: Paraffin waxes, among the most economical PCM sources, are frequently used for microencapsulation. They possess self-nucleating ability, no super-cooling effects, a high latent heat of fusion (over 250 kJ/kg), and a density of 0.93 kg/m^3. Paraffin waxes offer a broad melting point range (-5 to 76°C) and maintain their thermal storage ability through repeated cycles, making them suitable for both active and passive cooling of buildings. While their thermal conductivity is low (0.2-0.4 W/mK), this can be advantageous for insulation in building applications [11]. Paraffin's thermal conductivity can be further reduced using shell materials with low thermal conductivity, such as plastic polymers. Fire-resistant shell materials can address the low flash point concern (108-170°C) of paraffin waxes. Paraffin can also be blended with various materials to enhance structural and thermal properties [12,13].

3.2.2. Organic Non-Paraffins (Fatty Acids): Fatty acids are chosen as PCMs due to their abundant natural availability and cost-effectiveness compared to metal PCMs. They exhibit a high heat of fusion (up to 25 kJ/kg) and have a wide melting point range (7.8 to 127.2°C). Their low thermal conductivity (0.14 to 0.17 W/mK) makes them suitable for thermal insulation applications [14]. They typically have minimal super-cooling tendencies and may undergo solid-solid phase transitions in some cases. However, fatty acids have low flash points, making them susceptible to ignition. Impurities can affect their melting points, so pure fatty acids are essential for optimal thermal properties. They are less resistant to oxidizing agents, high temperatures, and flames, and some can be toxic and produce harmful fumes.

Commonly used fatty acids include stearic acid, palmitic acid, myristic acid, lauric acid, caprylic acid, capric acid, oleic acid, chosen based on specific application requirements [8].

3.3. Eutectics

Eutectic PCMs are typically comprised of a blend of two components with distinct melting points. Each component within this mixture exhibits congruent melting and freezing processes, forming crystals of the compound mixture. A notable advantage of eutectic PCMs is the ability to adjust the mixture's melting point to specific requirements by modifying the composition of each compound. These PCMs are known for their high energy storage density and thermal conductivity, with no congruent phase change and a lack of super-cooling effects. However, they have relatively low specific and latent heat capacities. One significant challenge is their potential for phase separation during repeated cycling, which can impact the thermo-physical properties of the eutectic mixture. Additionally, some eutectic blends may experience super-cooling issues. These materials tend to be relatively costly, and there is limited literature available on their thermo-physical properties [7, 15].

4. General Properties of PCM

Hydrated salts have high thermal conductivity and a high heat of fusion, making them suitable for certain applications. However, they are corrosive, with a melt temperature range from 0 to 100°C. Metallic PCMs have very high thermal conductivity and medium heat of fusion. They are heavy and stable over thermal cycling, making them suitable for applications requiring stability. However, their high cost can be a drawback. Paraffin PCMs have very low thermal conductivity, but they have a high heat of fusion. They are not corrosive and have a moderate weight, and they are stable over thermal cycling. Paraffins are cost-effective and have a melt temperature range from -20 to 100°C. Non-paraffin PCMs have low thermal conductivity and a high heat of fusion. They are mildly corrosive and have a moderate weight. While they are stable, they may decompose at high temperatures. However, they tend to be very costly [8].

5. Microencapsulation of PCM

A significant challenge when using phase change materials (PCMs) in various applications is the potential for leakage during phase transitions, which can reduce the material's effectiveness. Conventional PCMs also encounter issues like sub-cooling, decomposition, and corrosion [16]. To address these problems, encapsulation techniques are commonly employed to shield PCMs from external interactions. Encapsulation can occur at different scales: Macroencapsulation, microencapsulation, and nanoencapsulation. Microencapsulation, in particular, involves covering fine particles or droplets with a coating to create microcapsules. What makes microencapsulation widely accepted is its ability to encapsulate all states of matter (solid, liquid, and gas) using appropriate shell materials [17]. This method simplifies the handling of gases and liquids, making PCMs more versatile in various applications. Microencapsulation offers several advantages, including increased heat transfer area, reduced interactions between PCMs and the environment, and control over the volume changes that occur during phase transitions. The key to successful microencapsulation is the uniform and stable formation of the shell around the core, preventing internal component leakage. While microencapsulation is often used in fields aiming for targeted component release, in the case of microencapsulated PCMs (MEPCMs), the core must remain permanently enclosed within the shell, regardless of external forces [18].

5.1. Core and Shell materials for microencapsulation

The core material of microencapsulated phase change materials (MEPCMs) typically consists of phase change materials that undergo a process of absorbing and releasing energy during phase changes. The selection of the shell material is based on its compatibility with the core material and the surrounding environment. In heat transfer applications, a high thermal conductivity shell material is crucial to enhance heat performance [19]. Generally, inorganic materials exhibit higher mechanical strength and thermal conductivity compared to organic materials. MEPCMs can take on different structures depending on the core, shell, and encapsulation method used, including a single core enveloped by a continuous shell, multiple cores within a continuous shell, uniform dispersion of core material within the shell, and core coated with multiple layers of shell material (multi-walled capsules). Shell material stability is crucial for efficient encapsulation, as the shell should be strong enough to withstand stresses and phase change-induced volume changes [17]. Key requirements for shell materials include good barrier properties, protection from external environmental interactions, high-temperature applicability, corrosion resistance, mechanical strength, flexibility, ease of handling, and stable structure. Furthermore, shell materials should provide ample surface area for heat transfer, exhibit good thermal conductivity and diffusivity, remain inert to both the core material and the application environment, and withstand volume changes during phase transitions while remaining readily available, durable, and cost-effective.

Commonly used shell materials fall into several categories [20]:

5.1.1. Metallic Shell Materials: Used in very high-temperature applications, they offer high thermal stability, mechanical strength, and ease of fabrication, remaining intact even at temperatures up to 1000°C. However, they can be costly and susceptible to corrosion.

5.1.2. Organic Shell Materials: Frequently used for microencapsulating phase change materials, these materials are not suitable for heat transfer applications due to their poor thermal conductivity. However, they are widely employed for thermal insulation. Common materials include urea-formaldehyde (UF), melamine-formaldehyde (MF), polyurea, and acrylic resins. Organic shells offer good mechanical stability and resistance to volume changes during phase transitions.

5.1.3. Inorganic Shell Materials: Suitable for high-temperature applications, such as power generation and cement manufacturing, inorganic materials offer good mechanical strength, heat transfer performance, and thermal stability up to 1000°C. They are cost-effective compared to metallic shells. The main drawback is the porosity of the shell, which can lead to internal material leakage. Common inorganic shell materials include silica (SiO_2), sodium silicate, titanium dioxide, and calcium carbonate, with silicon dioxide being the most widely used. Surface modification is achievable with silica-based shell materials, and they are useful for controlling the flammable nature of organic core materials.

5.1.4. Hybrid Shell Materials: These materials combine both inorganic and organic elements to create superior stability and thermal conductivity. Incorporating nanoparticles of silver, iron, and silicon nitride into organic shells can enhance their characteristics. However, poor binding between the inorganic and organic components can be an issue, leading to detachment during repeated cycling. Techniques such as chemical hybridization can help mitigate this problem [21].

5.1.5. Plastics: Widely used due to their ease of fabrication and cost-effectiveness, plastics offer various physical and chemical methods for encapsulation. However, their poor thermal conductivity and limited thermal stability, up to a maximum of 400°C, can be limiting factors. Plastics are commonly used in applications like cooling of buildings, paper and food manufacturing, among others.

5.2. Various methods of microencapsulation

Selecting the appropriate core and shell materials and the most suitable method for creating effective microcapsules are crucial in developing high-quality microencapsulated phase change materials (MEPCMs). The choice of microencapsulation method is influenced by various factors, including cost, scalability, regulatory compliance, environmental impact, and health considerations [22]. The most commonly employed methods for microencapsulation include chemical methods, physico-chemical methods, and physico-mechanical methods. These methods often involve two key stages: emulsification and capsule formation. In emulsification, PCMs are finely dispersed in an aqueous phase, impacting the particle distribution and microcapsule size. The subsequent capsule formation stage relies on the cross-linking ability of the shell material surrounding the core. The type and amount of surfactant play a significant role in determining the size, stability, and formation process of microcapsules [23, 24]. Physical methods are also employed, but they tend to produce larger particles, typically above 100 μm, which may not be suitable for all applications.

5.2.1. Emulsion polymerization: Chemical methods, such as emulsion polymerization, are widely used for producing MEPCMs. For instance, in emulsion polymerization, which is also known as the solvent evaporation technique, the entire process consists of four stages. The core material is initially dispersed in a solvent, which is then emulsified in the presence of a surfactant in an aqueous phase. Subsequently, the solvent is evaporated, resulting in the formation of droplets around solid particles. In the final stage, the obtained solid particles are oven or vacuum dried to yield fine microencapsulated powders. The choice of solvent plays a crucial role, with properties like low toxicity, low boiling point, immiscibility with water, and high volatility being desirable. Dichloromethane has largely replaced the previously used chloroform. The particle size typically ranges from 0.5 to 5 μm, with an encapsulation ratio between 7% and 75% [25].

5.2.2. Dispersion polymerization: It is a straightforward single-stage method where reaction time, monomer and initiator amounts, and stabilizer concentration influence the final product's characteristics. Commonly encapsulated materials via this technique include alcohols, styrene in hydrocarbons, or alcohol mixtures with ether/water. This method allows for the successful encapsulation of hydrophilic core materials, such as PVA [26,27].

5.2.3. Suspension polymerization: This method is known for its cost-effectiveness and improved heat control during the entire process. The process involves mechanisms like monomer diffusion to the interface, secondary nucleation, particle break-up, and coalescence. These mechanisms collectively determine the properties, structure, and size of the resulting microcapsules [28]. The particle size can be estimated using a formula involving factors such as stirring speed, reaction temperature, and shell-to-core material ratio [29]. Parameters like stirring speed, temperature, and shell-to-core material ratio directly affect the thermal properties of the MEPCM.

5.2.4. Interfacial polymerization: It is a technique where an aqueous phase is prepared by dissolving the core material and various ratios of emulsifiers and stabilizers. The organic phase is then dispersed into the component-rich aqueous phase. This method can produce larger microcapsules, with sizes ranging from 20 to 30 μm in most industrial processes [30]. The solvent used for the core material should be non-reactive, and the first monomer should contain at least two organic compounds. The production parameters are easily controlled, and the maximum temperature reached during the process is around 80°C, which has a minimal impact on the PCMs [31]. However, the process has limitations, as most carrier materials are non-biocompatible and the organic solvents can contaminate the environment.

5.2.5. In situ polymerization: A three-stage process used to create microcapsules with shell materials like melamine-formaldehyde and urea-formaldehyde. This method is ideal for encapsulating a wide range of organic compounds as core materials [18]. The process begins with the formation of an oil-in-water emulsion containing the melted PCMs. Surfactants are added to stabilize the emulsion, and the emulsion is then stirred vigorously at a higher temperature. A cross-linking agent and nucleating agents are incorporated in the later stages. Maintaining a slightly acidic pH initiates the polycondensation reaction. The final microencapsulated material is then processed, cooled, washed, filtered, and dried to produce fine powdered MEPCMs [22, 32]. The size of the microcapsules ranges from 2 to 2000 μm. The reaction time is relatively short for polymers with high inherent reactivity, and this process results in uniformly coated microcapsules [25].

Physico-chemical methods offer a variety of techniques for microencapsulation of phase change materials (PCMs):

5.2.6. Sol-Gel Process: This technology, primarily used for silica shell development around PCMs, involves four stages. PCMs are initially emulsified with surfactants, creating an oil-in-water emulsion. In a separate sol solution, precursor materials for the shell (like tetraethoxysilane for silica) are dispersed in an acidic environment. The sol solution is slowly added to the emulsion under continuous heating and stirring. Shell formation occurs through polycondensation reactions. The resulting microcapsules are then filtered, washed, and dried. The process yields microcapsules with narrow particle size distribution (0.2-20 μm). While silica and titanium dioxide are common shell materials, high thermal conductivity can pose issues for building applications [25].

5.2.7. Coacervation: This older encapsulation technique includes simple and complex coacervation. In both cases, the process unfolds in three stages: first, core and shell material solutions are emulsified to create an oil-in-water emulsion. Then, oppositely charged colloidal solutions are added, causing the deposition of a polymer coating over the core. Adjusting pH is followed by thermal or chemical cross-linking for shell hardening. The product is cooled for further polymerization, recovered, and harvested as MEPCM. The particle size is efficiently controlled in this process, with factors such as core-to-coating ratio, emulsification time, and cross-linking agent quantity influencing efficiency. However, scaling up to an industrial process can be challenging [33].

***5.2.8. Supercritical CO_2-assisted Process*:** This method, used for essential oil extraction and more recent for encapsulating materials, which involves dynamic and static processes. In dynamic processing, the solution with the core material is premixed with supercritical CO_2 and rapidly expanded in a drying chamber. The static process features continuous mixing in low volume, expanding to atmospheric pressure after passing through a flow restrictor. The rapid expansion results in quick solvent evaporation and drying. This method is environmentally friendly and uses carbon dioxide as a solvent, offering advantages like non-toxicity and cost-effectiveness [34].

5.2.9. Self-Assembly Method: A cost-effective deposition process, the self-assembly method involves shell materials like Cu, Ca, or Na. In this technique, disordered components in a solution self-assemble into an organized structure through precipitation, forming a solid shell around the core. An oil-in-water emulsion, stabilized by mixed surfactants (commonly anionic and non-ionic), is created. Drop-wise addition of shell material into the emulsion, while maintaining agitation and temperature control, leads to shell deposition. The precipitated MEPCMs are recovered, washed, and vacuum-dried. Key factors in this process are the selection of surfactants that promote shell self-assembly and control over the precipitation and deposition of precursor materials at the oil-water interface [35].

Physico-mechanical methods offer various techniques for large-scale microencapsulation, but limitations in producing microcapsules smaller than 100 µm exist.

5.2.10. Electrospraying: This novel technology allows the creation of smaller microparticles and even nano-encapsulated PCMs. The technique involves spraying liquid shell and PCM materials onto a collector plate with a high electric field. Two separate syringes feed the materials through different nozzles at varying flow rates, with an adjustable voltage applied across the electrode. The resulting materials are collected, cured, washed, and dried to obtain microcapsules with core retention. It offers rapid, high-efficiency encapsulation with particle diameters ranging from 0.5 to 3 µm [36].

5.2.11. Spray Drying: Widely used and suitable for large-scale production, this method pumps a solution containing PCM, shell material, and a dispersing agent to an atomizer in a drying chamber filled with inert gas. Rotary atomization forms a fine spray, allowing solvent evaporation and the production of MEPCMs as fine powders. The method is versatile, cost-effective on a large scale, and easily scalable, with adjustable particle properties. However, high temperatures may damage the core, leading to particle agglomeration [37].

5.2.12. One-Step Method: This technique, known for self-stabilization and ease of industrial scaling, is versatile for various core materials and particle size tuning. It involves self-assembly, as demonstrated in stable MEPCMs with n-nonadecane as the core and silica as the shell. Self-stabilizing amine groups eliminate the need for additional stabilizers. Although it offers scale-up potential, more research is needed to enhance the final product's properties.

5.2.13. Air Suspension Coating: Similar to spray drying, this method suspends core materials in an upward-flowing airstream, with shell material sprayed over the suspended particles. The process involves handling around 20 variables, offering low production and large-volume handling capabilities, but it requires skilled labour and is mainly applied in food and pharmaceutical industries, with limited application in the PCM field.

5.2.14. Pan Coating: Used for larger capsules (greater than 600 μm), this technique coats solid core materials with atomized or solution-form shell material, then dries them to remove remaining solvent. Particle sizes of MEPCMs produced range from 600 to 5000 μm. The method's advantages include lower equipment costs, but challenges include low encapsulation efficiency and lengthy processing times [38].

5.2.15. Multi Orifice Centrifugal Process: Suitable for solid and liquid core materials, this process uses centrifugal force to pass the core materials through a membrane material, leading to microcapsule formation. Size varies from 5 to 1500 μm, but the high process temperature may affect heat-sensitive materials, and orifice clogging can be a concern.

5.2.16. Fluid Bed Coating: In this highly efficient coating process, shell material solution is sprayed into a hot, fluidized bed containing solid core materials. Two types, top-spray and bottom-spray coaters, are commonly used on an industrial scale. Both produce microcapsules with varied particle sizes. Proper control during drying is essential to prevent agglomeration [39].

5.3. Comparison of Encapsulation Techniques

The choice of encapsulation techniques is largely influenced by the type of core material and the intended application. It has been observed that as the core-to-shell ratio increases, the efficiency of encapsulation decreases. Methods such as complex coacervation and in-situ polymerization are capable of producing larger MEPCM particles with a high core material content, resulting in good encapsulation efficiency. Conversely, the emulsion or mini-emulsion polymerization technique is suitable for producing smaller MEPCMs. The smaller particle size is achieved by employing high stirrer speeds (ranging from 1000 to 13500 rpm) during emulsion dispersion and oil droplet formation. However, it's important to note that these techniques are relatively energy-intensive and costly. In contrast, the polymerization process typically operates at lower stirrer speeds (ranging from 300 to 600 rpm) and requires more time for particle generation, often up to 24 hours, especially when using silicon shell materials. Ensuring safety measures is essential to prevent interaction with any unreacted reagents after the cross-linking process. Methods such as self-assembly and the sol-gel method can effectively coat organic core materials with inorganic shell materials, resulting in good thermal properties and flame resistance. However, these inorganic shells may be less flexible compared to polymeric shells. MEPCMs with inorganic PCMs as core materials can only be generated through evaporation or solvent extraction methods. From an economic standpoint, MEPCMs with inorganic cores tend to be more expensive than those with organic cores due to the requirement for expensive solvents during synthesis. Furthermore, there is a risk that some solvents trapped inside the shell may leak out during repeated cycling, which is a notable drawback associated with this method.

Table 1. Properties associated with various encapsulation methods

Method of microencapsulation	**Encapsulation efficiency (%)**	**Core content (%)**	**Diameter (µm)**
Interfacial polymerization	71 – 87	29 – 80	0.5 – 1000
Phase separation method	66 – 75	43 – 75	0.5 – 1000
Emulsion polymerization	82.6	28 – 61	0.14 – 2.0
Complex Coacervation	80 – 95	26 – 67	2 – 1200
Phase separation method	66 – 75	43 – 75	0.5 – 1000
Sol-Gel encapsulation	82.0 – 90.7	46 – 74	2 – 30
Mini-emulsion polymerization	80.0 – 82.2	8 – 60	0.1 – 0.5
Solvent extraction/ Evaporation method methods	56 – 64	43 – 53	0.5 – 10

(Source: Su et al., 2015, [8])

5.4. Problems with microencapsulation of PCM

While microencapsulation is a widely accepted technique, it comes with certain drawbacks. Microencapsulated Phase Change Materials (MEPCMs) face limitations when employed in repeated cycling processes as thermal fluids due to increased viscosity resulting from the incorporation of larger microcapsules [18]. To address this issue, scientists are exploring Nano encapsulation, which produces smaller Nano-capsules. Supercooling is a common challenge in the widespread application of MEPCMs, where the crystallization temperature within the tiny shell material significantly differs from that in the core material within the shell and in the bulk. This disparity is often attributed to the insufficient number of nuclei within the tiny shell material, impacting the stable thermal application [40, 41]. Using organic materials like paraffin as PCMs presents a reduced thermal conductivity issue, which can be partially alleviated by increasing the heat transfer surface area, typically achieved through encapsulation. However, utilizing organic shell materials during encapsulation can further decrease thermal conductivity, making inorganic shell materials a more ideal choice due to their superior thermal conductivity and mechanical strength. Controlling the release of volatile organic compounds is crucial to maintain microsphere stability and ensure air quality, particularly in building applications. Organic PCMs are more susceptible to emitting these compounds, necessitating comprehensive studies before their application. Variations in particle morphology can also affect heat transfer properties, influenced by the type of emulsifiers used. High HLB value emulsifiers tend to result in agglomerated particles, while low HLB emulsifiers may lead to irregular surfaces with cracks or dents [42]. The choice of cross-linking agents can also impact the surface morphology of MEPCMs [43]. When hydrated salts are employed as MEPCMs, there is a risk of compound degradation during repeated cycling due to water gain or loss, considering their high latent heat energy [25]. The absence of standardized techniques for testing mechanical properties is a notable challenge, as it is essential to assess MEPCM leakage under pressure and external forces.

6. Advances in microencapsulation of PCM

As previously mentioned, overcoming supercooling is a critical challenge in expanding the practical use of Microencapsulated Phase Change Materials (MEPCMs). Researchers have developed various strategies to address this issue. Supercooling can be partially controlled through the addition of nucleating agents, which induce nucleation within the PCMs, and homogeneous nucleation induced by modifying the structure and composition of the shell material to encourage uniform nucleation. Common nucleating agents include nanoparticles, alcohols, and high freezing point paraffin to prevent supercooling. However, it's important to note that the poor thermal characteristics of the shell material can lead to a reduction in the thermal conductivity, impacting MEPCMs' efficiency. To enhance the thermal conductivity of MEPCMs, nanoparticles are added to the shell materials. Inorganic nanoparticles such as Carbon nanotubes, Graphene, TiO_2, Fe_3O_4, have been widely used to improve thermal conductivity [44, 45]. Traditional polymerization processes often involve high temperatures, which can affect the quality of certain PCMs. Modern low-temperature polymerization methods initiated using UV light have been developed to improve the quality of microspheres formed, although further research is needed in this area.

Despite significant advancements in MEPCMs, some challenges require more thorough investigation. While methods to address supercooling and enhance thermal conductivity have been developed, a well-defined and precise solution is still pending. Determining the lifespan of MEPCMs accurately is essential, and methods for extending their service life should be explored. Leakage issues resulting from reduced mechanical strength with repeated use also demand careful examination. In the case of slurries containing dispersed MEPCMs subjected to high shear forces during pumping, their stability during repeated cycling should be studied. Additionally, investigating the use of mixtures with varying melting points in the microencapsulation process could expand the temperature range and improve melting and solidifying properties [46]. It is crucial to design shell materials with high strength and temperature compatibility for high-temperature applications.

In efforts to mitigate supercooling issues, researchers have introduced nanoencapsulation techniques, which offer enhanced stability compared to microcapsules due to their smaller size and a lack of increased viscosity in the dispersion medium [47,48]. Nano-encapsulated Phase Change Materials (NEPCMs) are typically synthesized using methods like sol-gel, emulsion polymerization, and interfacial polymerization. These approaches have shown promising results in reducing supercooling problems associated with PCMs [49].

7. Conclusion

Microencapsulated Phase Change Materials (MEPCMs) represent an innovative approach to the realm of phase change materials, significantly enhancing their utility across various fields as a stable and effective solution. This technology involves creating stable microspheres that encapsulate core materials, thereby improving thermal, chemical, and physical stability. Common microencapsulation methods for PCMs include complex coacervation, sol-gel processes, in-situ and interfacial polymerization, spray drying, emulsion and suspension polymerization. The selection of a particular method is typically tailored to the specific application, core and shell material types, desired MEPCM size, and required physical, mechanical, and thermal properties. A wide range of materials has been successfully encapsulated using diverse shell materials through these processes, with designs tailored to meet specific application needs. MEPCMs can be applied in both high and low-temperature applications, depending on the choice of core and shell materials. Rigorous testing is essential to ensure that the produced microcapsules maintain quality and stability during repeated cycling. The MEPCM field has been gaining popularity due to its broad applicability, high stability, and extended service life. Various sectors, including waste heat recovery, building heating and cooling systems, electronics, textiles, packaging materials, heat pumps, and fabrics, benefit from the use of MEPCMs. Challenges such as supercooling and instability need to be addressed systematically to foster sustainable PCM development. Mitigating these issues can be achieved through the incorporation of nanoparticles, the development of nanoencapsulation techniques, and the utilization of multi-phase core materials. It is imperative to focus on continued research and investment in this industry to maximize energy recovery and reuse.

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