Formaldehyde-Free Phase Change Microcapsules: Green Design, Functionalization, and Application Progress

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Abstract. Phase change microcapsules (PCMs) represent an advanced functional material that encapsulates phase change materials within miniature protective shells. This unique characteristic endows them with significant application potential and value across diverse fields, including smart textiles, electronic thermal management, solar energy utilization, and healthcare. However, the traditionally widely used melamine-formaldehyde resin shell systems pose potential formaldehyde emission issues, which severely restrict their deployment in sensitive scenarios such as indoor environments, biomedical applications, and food engineering. This paper systematically reviews the research progress of formaldehyde-free phase change microcapsules, with a focus on environmentally benign shell material systems represented by acrylic resins, polyurethanes, polyureas, silica, and natural polymers, and their corresponding fabrication processes. It analyzes and compares the key properties of various formaldehyde-free microcapsules, including encapsulation efficiency, thermal performance, mechanical strength, and durability. The potential and adaptability of these materials in different application fields are also summarized. Finally, this paper discusses the current challenges in the industrialization of formaldehyde-free phase change microcapsule technology, such as cost containment, scalable production, and long-term stability. Prospects for future research directions are outlined, aiming to provide theoretical references and a systematic review for the development of next-generation safe and high-performance phase change materials.

Keywords: PCMs, formaldehyde-free, smart textiles.

1. Introduction

Energy scarcity stands as one of the critical challenges confronting humanity, with the imbalance between energy supply and demand becoming increasingly pronounced across temporal and spatial dimensions. Notably, substantial thermal energy is wasted during energy transmission processes. In recent years, phase change materials (PCMs) have been widely employed in thermal energy storage applications due to their ability to store or release large amounts of latent heat within a constant temperature range, thereby enhancing thermal energy utilization efficiency [1, 2]. However, bulk PCMs are prone to leakage during phase transitions. To address this issue in practical applications, microencapsulated phase change material (MEPCM) technology has emerged as a viable solution [3]. MEPCM technology involves encapsulating phase change materials within shells composed of organic or inorganic materials exhibiting high mechanical strength, thermal stability, and impermeability, resulting in nanoscale particles with stable core-shell structures [4, 5].

The MEPCM technology plays a significant role in advancing technological progress and promoting energy conservation across various industries. In the field of building energy conservation, MEPCMs with appropriate phase change temperatures and high latent heat values can be incorporated into mortar to enhance the thermal inertia of building structures, thereby reducing air conditioning energy consumption and meeting the energy efficiency requirements of green buildings [6]. In smart textiles, phase change microcapsules embedded in textile fibers or applied as surface coatings impart thermal buffering properties, enabling intelligent temperature regulation in outdoor sportswear. During extreme weather conditions or fluctuations in body temperature, garments integrated with phase change microcapsules can maintain constant skin temperature through heat absorption or release, providing long-lasting comfort to wearers [7]. To overcome the limitations imposed by the intermittency and dispersion of solar energy, phase change microcapsules are widely used as high-performance thermal storage media. They reduce energy loss and balance supply-demand by storing and releasing thermal energy, thereby significantly improving solar thermal efficiency [8]. By driving multiple industries toward green and low-carbon development, MEPCM technology has greatly enhanced energy utilization efficiency, directly reducing energy consumption and carbon emissions, and thus holds immeasurable value in promoting industrial upgrading and sustainable development.

Melamine-formaldehyde (MF) resin has long been the dominant shell material in academic and industrial circles due to its excellent film-forming properties, mechanical strength, and relatively low cost. However, the chemical structure of MF resin contains methylene linkages, which undergo slow hydrolysis or degradation in humid, hot, acidic, or alkaline environments, leading to continuous release of free formaldehyde [9]. Formaldehyde, a recognized carcinogen, causes severe irritation and damage to human eyes, nose, and respiratory systems. This formaldehyde emission risk has excluded traditional MF-based MEPCMs from sensitive application scenarios with strict VOC emission standards, such as indoor environments, medical devices, food engineering, and maternal-infant products, significantly limiting their market prospects [10]. Therefore, the development of high-performance, high-safety formaldehyde-free shell systems has become a key research topic in the MEPCM field during the current era of green development, with enormous market potential.

This paper aims to systematically review the latest research progress in formaldehyde-free phase change microcapsules, focusing on various environmentally benign shell material systems and their preparation processes. It analyzes and compares critical performance metrics, summarizes application potential, and discusses challenges in industrialization and future development directions, providing theoretical references and a comprehensive review for the development of next-generation safe and high-performance phase change materials.

2. Shell Materials of Formaldehyde-Free Phase Change Microcapsules

2.1. Acrylic Resin Shells

Acrylic resins are synthetic polymers formed by radical polymerization of acrylate and methacrylate monomers, exhibiting advantages such as diverse monomer selection, mature polymerization processes, high transparency, and excellent film-forming properties. As microcapsule shell materials, acrylic resins can form dense shell layers through in-situ polymerization, effectively encapsulating phase change materials [11]. By optimizing monomer ratios and polymerization processes, Li [12] demonstrated that acrylic resin-based microcapsules can achieve high encapsulation efficiency and thermal performance. However, these shell materials have certain limitations, including relatively limited heat resistance, brittleness of some homopolymers, and potential odor issues from certain monomers. To address these drawbacks, researchers typically employ copolymerization modification (e.g., introducing styrene, acrylonitrile monomers) or addition of inorganic nanomaterials (e.g., SiO_2, TiO_2) for improvement.

2.2. Polyurethane/Polyurea Shells

Polyurethane (PU) and Polyurea (PUrea) are polymeric materials formed by interfacial polymerization or in-situ polymerization reactions between polyisocyanates and polyol or polyamine monomers. These shell materials exhibit high reactivity, dense structure, excellent mechanical strength, toughness, and thermal stability, making them ideal choices for high-performance formaldehyde-free microcapsules. A prominent advantage of polyurethane/polyurea shells lies in their designability—mechanical and thermal properties can be precisely regulated by selecting isocyanates and alcohol/amine monomers with different structures.

Active Flow Focusing (AFF) technology enables the production of droplets with high accuracy and controllability while achieving high-throughput manufacturing, suitable for various fluid types including organic and inorganic fluids. Shell thickness can be controlled by adjusting monomer ratios, and droplet size can be precisely regulated by modifying phase flow rates and excitation frequencies. Li et al. [13] utilized a universal liquid-driven active flow focusing platform to adjust the diameter of

PCMCs, with shell thickness controlled via monomer ratio optimization. In synchronized state, droplet size depends solely on flow rate and excitation frequency, which can be accurately predicted by scaling laws. The prepared PCMCs exhibit uniform particle size with a coefficient of variation (CV) below 2%, featuring smooth surfaces and compact structures. However, high-performance isocyanate monomers incur higher costs and are sensitive to moisture in raw materials, requiring strict process control during preparation.

2.3. Silica Shells

Silica (SiO_2) represents inorganic shell materials, primarily prepared via sol-gel method through hydrolysis and condensation of precursors such as tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS). Inorganic SiO_2 shells offer exceptional thermal stability, chemical inertness (high temperature resistance, oxidation resistance, non-flammability), high shell compactness, and non-toxicity, making them suitable for high-temperature applications. However, SiO_2 shells have obvious drawbacks: inherent brittleness of inorganic layers leads to easy rupture under external forces (extrusion, friction), causing PCM leakage, which severely limits their use in applications requiring mechanical processing.

To address this issue, researchers have attempted organic-inorganic hybrid strategies by compounding SiO_2 with flexible polymers. The SiO_2 shell not only prevents leakage of hydroxyl-containing fibers but also enhances thermal conductivity. Zhang et al. [14] successfully embedded black 300 nm Ti_4O_7 particles into SiO shells, resulting in paraffin@SiO_2/Ti_4O_7 microcapsules that retain most of the paraffin's enthalpy, improve stability, and exhibit excellent thermal energy storage performance. When the mass fraction of Ti_4O_7 nanoparticles reaches 3 wt% relative to paraffin, the photothermal storage efficiency of these microcapsules reaches 85.36%, compared to only 24.14% for pure paraffin. This highlights the significant advantage of such shell materials in efficiently utilizing abundant solar energy resources.

2.4. Natural Polymer Shells

Natural polymer shells are derived from biomass, such as chitosan (CS), Gum Arabic, and Sodium Alginate. These materials offer core advantages including biodegradability, excellent biocompatibility, absolute safety, renewable raw materials, and environmental friendliness, endowing them with irreplaceable value in food and medical fields. Gao et al. [15] successfully prepared novel chitosan-polyurethane (c-PU) MicroPCMs through interfacial polymerization of hexamethylene diisocyanate (HMDI) and chitosan (CS) assisted by charge attraction. The application of natural non-toxic CS in MicroPCMs explored a new pathway for green shell preparation.

However, natural polymers typically exhibit poor mechanical strength, inferior barrier properties compared to synthetic polymers, susceptibility to microbial effects, and performance sensitivity to environmental humidity. To solve these problems, crosslinking modification (e.g., with glutaraldehyde, genipin) or compounding with other materials is commonly used to enhance their performance.

3. Performance Analysis and Comparison

3.1. Natural Polymer Shells

Thermal cycling stability is a critical indicator for evaluating the practicality of microcapsules, as it reflects the ability of microcapsules to maintain encapsulation integrity and thermal performance during repeated phase change cycles. The thermal performance of formaldehyde-free phase change microcapsules primarily includes key indicators such as phase change enthalpy (latent heat value), phase change temperature, thermal cycling stability, and thermal conductivity. Phase change enthalpy determines the heat storage capacity of microcapsules, while phase change temperature defines their applicable temperature range. Studies have demonstrated that microcapsules with different shell material systems exhibit significantly distinct thermal performance, which is closely related to their chemical structures and micro-morphologies.

Polyurethane/polyurea (PU/PUrea) shell microcapsules typically possess high phase change enthalpy (160-190J/g) and excellent thermal cycling stability, attributed to the flexibility of urethane bonds in their molecular chains. For instance, butyl stearate/polyurethane microcapsules with a core-to-shell ratio of 3:1 maintain an enthalpy retention rate of up to 92% after 1000 thermal cycles. The underlying mechanism lies in the microphase-separated structure of polyurea molecular chains-rigid segments form physical cross-linking points, while flexible segments buffer the phase change-induced stress-effectively suppressing the leakage of core materials.

Acrylic resin shell microcapsules exhibit a slightly lower phase change enthalpy (150-180J/g), but their ester groups demonstrate good compatibility with core materials. Through emulsion polymerization, the shell thickness can be precisely controlled within 5-10μm, achieving an enthalpy retention rate of 85% after 600 thermal cycles.

Silica (SiO_2) shell microcapsules generally have lower phase change enthalpy (120-160 J/g) due to the high-density packing of inorganic siloxane networks (—Si—O—Si—), but they excel in thermal stability. The MF/SiO_2 hybrid shell microcapsules prepared by the team from Shenzhen University exhibit a 30.05% increase in thermal conductivity via the inorganic thermal conduction network constructed by the sol-gel method, and they maintain structural integrity even at 200°C. This phenomenon originates from the "pinning effect" of SiO_2 nanoparticles on polymer chains and their pore-filling function.

Natural polymer shell microcapsules (e.g., chitosan-based) have the lowest phase change enthalpy (100-150J/g). However, the hydroxyl groups in their molecular chains can form hydrogen bond networks, endowing them with excellent environmental compatibility during biodegradation, making them particularly suitable for disposable medical products [16].

3.2. Long-Term Durability

Long-term durability is a comprehensive indicator for evaluating the practicality of formaldehyde-free phase change microcapsules, encompassing thermal stability, chemical stability, and mechanical stability. For formaldehyde-free microcapsules, the ability to retain performance during long-term service is of great significance, as it directly determines the service life and reliability of the material. Accelerated aging tests are commonly used to assess the long-term durability of microcapsules, simulating long-term service conditions under harsh environments such as high temperature and high humidity.

Polyurea/SiO_2 hybrid shell microcapsules exhibit outstanding durability. In the QUV accelerated aging test (cycling between 8 h of UV exposure at 60°C and 4 h of condensation at 50°C), the polyurea coating modified with 1.5% nano-SiO_2 showed a 120 h delay in entering the rapid aging stage compared to pure polyurea, and maintained an enthalpy retention rate of 85% after 720 h of aging. The underlying mechanisms include: (1) Nano-SiO_2 particles fill the gaps between polyurea molecular chains, enhancing the coating density; (2) Silanol groups (—SiOH) form hydrogen bonds with the amino groups of polyurea, inhibiting the oxidative degradation of molecular chains; (3) The "rigid support" effect of nanoparticles reduces microcrack formation caused by thermal expansion and contraction.

In the 3.5% NaCl solution immersion test, the electrochemical impedance modulus of this hybrid shell was increased by one order of magnitude compared to pure polyurea, and the corrosion potential shifted from -40 mV to 60 mV, extending the immersion service life by over 600h—confirming its excellent chemical stability [17].

4. Analysis of Application Fields

4.1. Smart Textiles

In the field of smart temperature-regulating textiles, formaldehyde-free phase change microcapsules impart adaptive temperature regulation capabilities to textiles by being embedded in fibers or applied as fabric coatings, and are widely used in outdoor clothing, sportswear, and medical textiles. For this application, flexibility, wash resistance, and skin contact safety are key considerations.

The chitosan-SiO_2 composite microcapsules (PEO@CS-SiO_2) developed by the research team from Jiangnan University exhibit excellent fabric applicability, with the UPF (Ultraviolet Protection Factor) value remaining at 65.1 after 50 dry rubbing cycles. The core mechanism involves silane coupling agent (IPTS)-mediated Si-O-C covalent bonds, which anchor the microcapsules to the surface of cotton fibers and significantly enhance interfacial adhesion.

Polyurethane shell microcapsules, relying on the hydrogen bonding between their -COO- groups and fibrous proteins, maintain an enthalpy retention rate of 80% after 20 standard washing cycles, with a tensile strength of 10.98 MPa—meeting the mechanical stress requirements of textile processing. In terms of application processes, the melt-blending spinning method enables uniform embedding of microcapsules inside fibers (with particle size controlled at 5-20 μm), while the coating method constructs a 30–50 μm functional layer via foam finishing. The appropriate method should be selected based on the type of fabric [7, 8].

4.2. Building Energy Conservation

In the field of building energy conservation, formaldehyde-free phase change microcapsules can be incorporated into building structures such as gypsum boards, cement-based materials, and thermal insulation materials. They regulate indoor temperatures by storing and releasing latent heat, thereby reducing air conditioning energy consumption and improving building energy efficiency. For this application, long-term durability, compatibility with building materials, cost, and thermal stability are key considerations.

Acrylic resin shell microcapsules are preferred for large-scale applications due to their raw material cost—only 1/3 of that of polyurea. When added at 20 wt%, the average surface temperature of cement-based composites decreases by 4.9°C under the same heating conditions, and the maximum temperature drop of single-sided heat storage walls near the phase change point reaches 6.2°C.

SiO_2 shell microcapsules modified with 5% nano-SiO_2 exhibit an increased melting temperature of 120.7°C, but their brittleness needs to be addressed. Modification with the silane coupling agent KH550 increases the thickness of the interfacial transition zone between microcapsules and the cement matrix from 10μm to 25μm, improving compressive strength by 20%. Optimization experiments show that a microcapsule addition amount of 15–20 wt% achieves a balance between performance and cost, reducing the thermal conductivity of the composite by 15–20% compared to pure cement [18].

4.3. Electronic Thermal Management

As electronic devices trend toward high performance and miniaturization, thermal management has become a critical technology for ensuring device reliability. Composite phase change materials based on $In_{51}Bi_{32.5}Sn_{16.5}$@$SiO_2$ microcapsules can be used to prepare flexible thermal interface materials, effectively managing transient thermal shocks in electronic devices (e.g., CPUs, LEDs, and battery packs). For this application, high reliability, high thermal conductivity, and anti-leakage performance are key considerations.

The high density of SiO_2 shells (porosity < 3%) is the core guarantee for anti-leakage. Their amorphous structure allows uniform shell thickness control at 7.5μm by adjusting the sol-gel reaction temperature (50–80°C). Although the thermal conductivity of the $In_{51}Bi_{32.5}Sn_{16.5}$ alloy core reaches 20 W/(m·K) (a typical value for metal alloys), the thermal conductivity of the SiO_2 shell itself is only

1.3–1.4 W/(m·K). Therefore, it is necessary to optimize the particle size distribution (D50 = 5μm) to reduce interfacial thermal resistance. Studies have shown that when the microcapsule volume fraction is 30%, the thermal conductivity of the composite reaches 1.5 W/(m·K)—a 300% increase compared to pure polymer matrices—and remains stable during thermal shock cycles of -40~120°C [19].

4.4. Biomedical Field

In the field of biomedical antibacterial applications, the unique value of silver/silica (Ag/SiO_2) double-shell multifunctional phase change microcapsules lies in their integration of antibacterial effects with thermal energy storage and electrical conductivity, meeting the demand for "antibacterial + multi-performance synergy" in this field.

The Ag@SiO_2 microcapsules exhibit a minimum inhibitory concentration (MIC) of only 1.96 μg/mL against Staphylococcus aureus and a bactericidal rate of nearly 100%. Their porous SiO_2 shells (pore size: 2–5 nm) enable controlled release of silver ions via diffusion (release cycle > 14 days), avoiding the burst release issue of traditional silver-based agents. In terms of electrical properties, when the Ag content is 5 wt%, the electrical conductivity of the composite microcapsules reaches 10^{-4} S/cm—meeting the requirements for bioelectrical signal transmission—due to the hopping electron transport mechanism of silver nanoparticles in the SiO_2 network [20].

5. Conclusion

This paper systematically reviews the research progress of formaldehyde-free phase change microcapsules, focusing on analyzing the performance characteristics, preparation processes, application fields, and industrialization challenges of four main types of formaldehyde-free shell materials: acrylic resins, polyurethane/polyurea, silica, and natural polymers. Research demonstrates that formaldehyde-free phase change microcapsule technology has developed multiple reliable pathways, with various formaldehyde-free shell systems exhibiting distinct performance characteristics. These systems are expected to replace traditional MF microcapsules in different fields, meeting the market's higher demands for safety and environmental friendliness.

However, formaldehyde-free phase change microcapsules still face industrialization challenges including performance balance, cost control, large-scale production, and long-term stability. Future research should focus on developing new low-cost materials, designing multifunctional composite shell materials, utilizing advanced computational methods to guide material design, and establishing standardized testing and evaluation systems. Through interdisciplinary collaboration and in-depth integration of industry, academia, and research, formaldehyde-free phase change microcapsule technology is expected to achieve greater breakthroughs in the near future, providing more advanced and safer solutions for sustainable energy management and intelligent material applications.

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