Postprint: Study on Influencing Factors in the Preparation of Double-Shell Micro-Nano Phase Change Capsules

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Abstract

Double-shell micro/nano phase change capsules were prepared via miniemulsion interfacial polymerization using phase change material as the core, polystyrene as the inner shell, hydrophilic chitosan as the outer shell, sodium dodecyl sulfate as the emulsifier, hexadecane as the co-emulsifier, and azobisisobutyronitrile as the initiator, with a shell-to-core ratio of 1:1. The capsules were characterized by FT-IR, DSC, SEM, and LPSA, and the effects of core material type, emulsifier dosage, co-emulsifier dosage, initiator dosage, ultrasonic emulsification time, and stirring speed on their morphology were investigated. The results indicate that the morphology of the double-shell micro/nano phase change capsules is significantly influenced by the core material type, emulsifier dosage, co-emulsifier dosage, and initiator dosage, and is also related to the ultrasonic emulsification time and stirring speed, with corresponding optimal process parameters obtained.

Full Text

Study of Influential Factors in Double-Shell Phase Change Micro-Nano Capsules Preparation

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Abstract

Double-shell phase change micro-nano capsules were prepared via miniemulsion interfacial polymerization using phase change materials as the core, polystyrene as the inner shell, and hydrophilic chitosan as the outer shell, with a core-to-shell ratio of 1:1. Sodium dodecyl sulfate served as the emulsifier, hexadecane as the co-emulsifier, and azodiisobutyronitrile as the initiator. The prepared capsules were characterized by Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and laser particle size analysis (LPSA). The effects of core material type, emulsifier dosage, co-emulsifier dosage, initiator dosage, ultrasonic emulsification time, and stirring speed on the morphology of the double-shell phase change micro-nano capsules were investigated. The results demonstrate that capsule morphology is significantly influenced by the core material type and the amounts of emulsifier, co-emulsifier, and initiator, and is also related to ultrasonic emulsification time and stirring speed. The corresponding optimal process parameters were determined.

Keywords: organic polymer materials, double-shell phase change micro-nano capsules, miniemulsion interfacial polymerization method, morphology, particle size, influential factors

Microencapsulation technology employs film-forming materials to encapsulate solids or liquids into core-shell structured particles known as microcapsules. Microencapsulated phase change materials (PCMs) consist of a phase change core and a coating shell. During phase transition, the encapsulated PCM undergoes phase change while the outer polymer shell remains solid. This solves the fluidity problem of phase change materials during transition and expands their application scope. The core-shell structure isolates the encapsulated material from the external environment, enhancing the core' s stability and durability [1-2].

With the maturation and deepening of microencapsulation technology, nanocapsules have developed rapidly. Nanocapsules represent a novel type of microcapsule with nanoscale dimensions, typically ranging from 1-1000 nm in diameter. The reduction from micrometer to nanometer scale provides a larger specific surface area, which enhances the heat transfer rate of phase change materials and significantly reduces damage caused by inter-particle collisions. G. Fang et al. [4] prepared microcapsules using n-tetradecane as the core and polyurea as the shell material via in-situ polymerization, achieving a phase change latent heat of 134.16 kJ/kg. Zou et al. [5] used an aqueous solution of polyoxyethylene octylphenyl ether as emulsifier and obtained n-hexadecane microencapsulated PCMs through interfacial polymerization triggered by adding diamine to toluene diisocyanate (TDI), with phase change latent heat of 48-66 kJ/kg. Y. Taguchi et al. [6] employed suspension polymerization with methyl methacrylate as the monomer to encapsulate n-pentadecane PCM, producing nanocapsules with phase change latent heat of 97-107 kJ/kg.

Encapsulating phase change core materials offers several advantages [7-10]: (1) increased specific surface area and thermal conductivity; (2) completion of phase transition within capsules, eliminating phase separation and supercooling phenomena; (3) enhanced stability of PCMs, reduced toxicity of certain materials, and elimination of surface frosting issues in building materials; (4) improved durability and extended service life; and (5) convenient packaging that meets green building material requirements.

However, both micro- and nano-phase change capsules suffer from the limitation of single functionality—temperature regulation only. Indoor applications can adjust temperature but not humidity, failing to improve indoor environmental comfort or fundamentally achieve building energy efficiency. Therefore, developing micro/nano phase change capsules with excellent performance, stable processing, and dual temperature-humidity regulation functions represents both an urgent requirement for building energy conservation and a key research challenge in multifunctional capsule development. Shang Jianli et al. [11] prepared composite microcapsules with temperature and humidity regulation capabilities using in-situ and interfacial polymerization methods, with paraffin as the core, highly oil-absorbent polyacrylate as the inner shell, and highly water-absorbent sodium polyacrylate as the outer shell. However, these composite microcapsules exhibited large particle sizes and poor morphology, lacking systematic analysis of preparation parameters.

In view of this, this study utilizes the characteristics of PCM capsule wall materials, particularly the relationship between organic polymer chemical/physical structures and water molecule adsorption [12], to prepare double-shell micro-nano phase change capsules with dual temperature-humidity regulation functions by encapsulating hydrophilic polymer materials outside existing shells. The preparation process parameters were optimized, and the main factors influencing the morphology of double-shell micro-nano phase change capsules and their interrelationships were thoroughly investigated.

1 Experimental Methods

1.1 Materials

The main raw materials included: n-octadecane ($C_{18}H_{38}$, analytical grade); n-dodecanol ($C_{12}H_{26}O$, analytical grade); styrene (St, analytical grade); methyl methacrylate (MMA, analytical grade); butyl acrylate ($C_7H_{12}O_2$, analytical grade); acrylic acid (C_3H_4O, analytical grade); chitosan (water-soluble, 85% deacetylation); hexadecane ($C_{16}H_{34}$, analytical grade); sodium dodecyl sulfate (SDS, analytical grade); azodiisobutyronitrile (AIBN, chemically pure); divinylbenzene (analytical grade, 80% purity); tetraethylenepentamine (TEPA, analytical grade). All experimental water was deionized.

1.2 Preparation Process

Prior to experiments, styrene (St) and methyl methacrylate (MMA) were washed with 10% sodium hydroxide solution to remove inhibitors. Using the miniemulsion interfacial polymerization method [13], the core material (n-dodecanol or n-octadecane), main monomer (styrene), methyl methacrylate, co-emulsifier (hexadecane), initiator (azodiisobutyronitrile), and divinylbenzene were mixed uniformly to obtain the oil phase. A specified amount of emulsifier was dissolved in deionized water and stirred for 10 min to obtain the aqueous phase. The oil phase was added to the aqueous phase and pre-emulsified for 5 min at 40°C using an electric mixer at a certain speed. The resulting pre-emulsion was then ultrasonically dispersed for 10 min at 150 W power with 2 s intervals in an ice-water bath using an ultrasonic cleaner to form a uniform fine emulsion.

The fine emulsion was transferred to a four-neck flask equipped with a reflux condenser, mechanical stirrer, and thermometer. Under constant stirring, an appropriate amount of 1% acetic acid chitosan solution and tetraethylenepentamine were slowly added via a dropping funnel. The reaction proceeded at 40°C for 4 h, after which the temperature was increased to 80°C for an additional 4 h. Upon completion, the mixture was naturally cooled to room temperature to obtain the double-shell phase change micro-nano capsule emulsion. The prepared emulsion was vacuum-filtered, and the filter cake was washed once with 100 ml of 25% ethanol and twice with hot water, followed by vacuum drying to obtain the double-shell phase change micro-nano capsules.

1.3 Performance Testing

Thermal storage performance testing: The phase transition temperature and latent heat of the double-shell phase change micro-nano capsules were measured using a DSCQ1000V9.0 thermal analyzer. The temperature range was -20 to 60°C, with heating and cooling rates of 10°C/min under N_2 atmosphere. Based on DSC results, the mass fraction of phase change material in the capsules was calculated as [14]:

$$\text{Mass fraction (\%)} = \frac{H_P}{H_W} \times 100\%$$

where H_W and H_P represent the latent heat measured by DSC for the capsules and pure phase change material, respectively. The encapsulation efficiency of the phase change material was calculated using the mass fraction in capsules and the initial core material mass fraction:

$$\text{Encapsulation efficiency (\%)} = \frac{X}{W} \times 100\%$$

where X is the mass fraction of phase change material in the capsules and W is the initial mass fraction of core material.

Moisture absorption/desorption performance testing: The moisture performance of double-shell phase change micro-nano capsules was tested under five relative humidity environments (Table 1), ranging from 11.3% to 97.3%. Analytically pure solid salts and distilled water were used to prepare saturated solutions, maintaining 30% undissolved solid salt. Solutions were prepared at 50°C to ensure full saturation. After salt precipitation, solutions were cooled to 25°C. Prior to testing, samples were dried in an oven until three consecutive measurements at 24 h intervals showed mass differences less than 0.1%, indicating complete dryness. Dried samples were placed above saturated salt solution barriers in desiccators for 14-21 days to reach equilibrium. After equilibrium, samples were weighed and transferred to another humidity environment. This process was repeated, periodically measuring and recording sample mass at equilibrium for each humidity condition. The equilibrium moisture content u (kg/kg) was calculated as [15]:

$$u = \frac{m - m_0}{m_0}$$

where m_0 is the mass of the dry material (kg) and m is the mass after moisture absorption (kg).

Sample characterization: The structure of double-shell phase change micro-nano capsules was analyzed using a BRUKER UECIOR22 FT-IR spectrometer. Dried capsule samples were mixed with potassium bromide and pressed into pellets for testing at 25°C with absorption spectra from 4000-500 cm^{-1}. Morphology was observed using a Quanta200 SEM (operating voltage: 0-25 kV). Capsules were fixed on sample stages and sputter-coated with gold before testing (resolution: 1 nm). Particle size was measured using a NANOPHOX laser particle size analyzer. Capsules were dissolved in dispersion liquid, ultrasonically dispersed, and tested with a refractive index of 1.421.

2 Results and Discussion

2.1 Structure of Double-Shell Phase Change Micro-Nano Capsules

Figure 1 [Figure 1: see original paper] presents the FT-IR spectra of methyl methacrylate, chitosan, and double-shell phase change micro-nano capsules. Figure 1a shows the methyl methacrylate spectrum, with a C-H stretching vibration peak of the C=C-H group near 2999.02 cm^{-1} and an ester C=O stretching vibration at 1723.16 cm^{-1}. Figure 1b shows the chitosan spectrum, with N-H bond stretching vibration near 1250.95 cm^{-1} and C=O bond stretching vibration near 779.27 cm^{-1}. For the double-shell capsules (Figure 1c), peaks near 2921.28 cm^{-1} correspond to C-H stretching of -CH_2 groups, while the characteristic ester C=O stretching absorption appears at 1729.26 cm^{-1}. Additionally, a peak near 759.92 cm^{-1} represents -CH_2- rocking absorption, indicating good grafting of methyl methacrylate and chitosan onto the outer shell. The absence of polystyrene absorption peaks in Figure 1c confirms that polystyrene constitutes the inner shell rather than the outer shell. Based on this analysis, the double-shell phase change micro-nano capsules possess a double-shell structure with polystyrene as the inner shell and hydrophilic chitosan as the outer shell.

2.2 Factors Influencing Capsule Morphology

2.2.1 Effect of Core Material Type The core material of double-shell phase change micro-nano capsules undergoes solid-liquid or solid-solid phase transitions with temperature changes. As the heart of the capsules, the core must absorb or release substantial latent heat. Core material selection affects not only temperature regulation performance but also the degree of shell encapsulation. While many materials can serve as core materials, this study selected polystyrene for the inner shell due to its controllable reaction and wide temperature range, and chose polymethyl methacrylate (for its chemical stability and impact resistance) grafted with chitosan (for its sustained-release properties and biocompatibility) for the outer shell. Literature suggests a 1:1 core-to-shell ratio is optimal for capsule formation [16].

Comparative experiments using n-dodecanol (alcohol) and n-octadecane (paraffin) as core materials revealed significant differences. Capsules prepared with n-dodecanol (Figure 2a [Figure 2: see original paper]) showed low yield, irregular 堆积 morphology, large particle sizes, and poor uniformity. In contrast, capsules with n-octadecane (Figure 2b) exhibited high yield, spherical morphology, micro-nano scale coexistence, dense structure, and good integrity.

2.2.2 Effect of Emulsifier Dosage Emulsifiers primarily function as dispersing, stabilizing, and solubilizing agents, transforming oil-water mixtures into emulsions. When dispersed on the dispersed phase surface, emulsifiers form films or electrical double layers that impart charge to the dispersed phase, preventing droplet coalescence and creating stable emulsions for proper capsule formation. This study used sodium dodecyl sulfate as the emulsifier, investigating its dosage (1%, 2%, 3%, and 5% by mass fraction) on capsule morphology.

Results showed that at 1% and 5% emulsifier, capsules exhibited visibly large particle sizes, non-spherical shapes, and severe agglomeration. The mechanisms [17-18] are: (1) At low emulsifier dosage, incomplete adsorption on the dispersed phase surface creates strong inter-droplet forces, causing adhesion and gel formation. (2) At high dosage, excessive surface coverage reduces interfacial tension differences between shell/water and core/water interfaces. Since core/shell interfacial tension remains constant, reduced interfacial energy leads to irregular capsule formation.

At 2% emulsifier (Figure 3a [Figure 3: see original paper]), capsules showed complex morphology with few spherical particles, large and non-uniform sizes, persistent agglomeration, and surface defects. At 3% emulsifier (Figure 3b), capsules displayed smooth, dense surfaces without obvious defects, with nearly all particles showing good sphericity, small size, and excellent uniformity.

2.2.3 Effect of Co-Emulsifier Dosage Co-emulsifiers adjust the HLB value of emulsifiers, reducing oil-water interfacial tension and creating interfacial barriers that slow monomer migration from small to large droplets while facilitating dispersion into smaller droplets. This study used hexadecane as the co-emulsifier, investigating its dosage (0.1%, 0.3%, and 0.6% mass fraction) on particle size.

At 0.1% co-emulsifier (Figure 4a [Figure 4: see original paper]), insufficient HLB adjustment left small droplets incompletely coated by emulsifier, increasing coalescence probability and resulting in large capsule sizes (>100 µm) [19]. At 0.6% (Figure 4c), capsules also showed large sizes (~100 µm) due to excessive hydrophobic organic volatile substances adversely affecting the final miniemulsion performance [20]. At 0.3% (Figure 4b), capsule size decreased significantly with better uniformity, primarily distributed in the 100-1000 nm range, with approximately half the capsules measuring 200-300 nm. This intermediate dosage provided optimal miniemulsion stability, facilitating proper capsule formation.

2.2.4 Effect of Initiator Dosage Initiators, also called free radical initiators, generate radicals to initiate polymerization. This study used azodiisobutyronitrile as the initiator for emulsion free radical polymerization, investigating its dosage (0.5%, 1.0%, and 2.0% mass fraction) on capsule morphology (Table 2).

At 0.5% initiator, almost no capsules formed due to low monomer conversion in latex particles and nearly equivalent monomer transfer between particles. At 1.0% initiator, the emulsion showed good stability, producing capsules with most particles uniformly distributed at 200-300 nm and high phase change enthalpy of 67.77 kJ/kg. Increased initiator dosage leads to unequal, random monomer transfer through particle collisions, broadening size distribution [21]. Theoretically, an optimal initiator dosage exists that initiates all latex particles equally, yielding narrow size distribution. However, at 2.0% initiator, massive agglomeration occurred due to runaway polymerization.

2.2.5 Effect of Ultrasonic Emulsification Time Ultrasonic emulsification is a critical step in miniemulsion polymerization, using high shear forces to disperse the oil phase into nanoscale core droplets. This study investigated emulsification time (5 min, 10 min, 15 min) on capsule morphology.

At 5 min (Figure 5a [Figure 5: see original paper]), capsules appeared yellow with extremely irregular morphology and large particles. At 15 min (Figure 5c), significant improvements in color, morphology, and particle size were observed compared to 5 min. At 10 min (Figure 5b), capsules formed fine powders with uniform particle size distribution and regular shapes, though minor agglomeration persisted, meeting micro-nano scale requirements.

2.2.6 Effect of Stirring Speed Three forces act on the dispersed phase [22]: (1) shear stress, (2) surface tension, and (3) internal viscous stress. Shear stress causes droplet dispersion, while the other two forces resist it. When shear stress exceeds resistance, droplets continuously split. Since shear stress is proportional to stirring speed, increased speed disperses droplets finer, but excessive shear can cause emulsion loss and incomplete reaction. Continuous stirring also enables droplet re-coalescence. To prevent merging and generate uniform particles, turbulence must reach a certain intensity. Therefore, appropriate stirring speed is crucial for dispersion and directly affects capsule formation.

This study investigated stirring speeds of 500, 800, and 1000 r/min. As shown in Figure 6 [Figure 6: see original paper], increasing speed produced more irregular spherical particles due to demulsification and splashing, with residual emulsion on flask walls causing incomplete reaction and large irregular capsules. At 500 r/min (Figure 6a), the emulsion reacted completely, producing capsules with complete morphology and dense structure.

2.3 Performance Analysis of Double-Shell Phase Change Micro-Nano Capsules

Based on the above analysis, the optimal process parameters for preparing double-shell phase change micro-nano capsules with polystyrene inner shell and hydrophilic chitosan outer shell are: n-octadecane as core material, core-to-shell ratio of 1:1, 3% emulsifier, 0.3% co-emulsifier, 1.0% initiator, 10 min ultrasonic emulsification, and 500 r/min stirring speed. Capsules prepared under these conditions were tested for thermal storage and moisture absorption/desorption performance.

As shown in Figure 7 [Figure 7: see original paper], the capsules exhibit a phase transition temperature of 30.01°C with a broad transition range of 20-40°C and latent heat of 67.77 kJ/kg. This indicates the capsules respond well to indoor temperature variations and can effectively reduce temperature fluctuations for improved comfort. The core material n-octadecane has a phase transition temperature of 31.7°C and latent heat of 218 kJ/kg. Using the formula from Section 2.3.1, the mass fraction of PCM (n-octadecane) in the capsules is 31.1%, with an encapsulation efficiency of 62.2%.

Figure 8 [Figure 8: see original paper] demonstrates that the double-shell capsules possess stronger moisture absorption/desorption performance compared to conventional inorganic porous materials (e.g., building gypsum) [23]. This is attributed to the outer shell composed of methyl methacrylate grafted with chitosan, where the hydrophilic chitosan contains functional groups with strong water affinity. While building gypsum has some moisture capacity through micropore adsorption, its effect is limited. However, the capsules still exhibit the common issue of humidity-control materials: under isothermal conditions at the same relative humidity, the equilibrium moisture content during desorption exceeds that during absorption.

3 Conclusions

1. Methyl methacrylate and chitosan graft effectively onto the outer shell of double-shell phase change micro-nano capsules, successfully encapsulating the polystyrene inner shell and PCM core to form a double-shell structure.
2. The optimal process parameters for preparing double-shell phase change micro-nano capsules are: n-octadecane core, core-to-shell ratio of 1:1, 3% emulsifier, 0.3% co-emulsifier, 1.0% initiator, 10 min ultrasonic emulsification, and 500 r/min stirring speed.
3. Capsules prepared with optimal parameters show most particles distributed between 200-300 nm, achieving micro-nano scale coexistence, good sphericity, dense structure, and high thermal storage and moisture absorption/desorption performance.

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