Review of Encapsulated Salt Hydrate Core-Shell Phase Change Materials†

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Abstract

The salt hydrate heat storage phase change material (PCM) has a promising prospect of application and has become a research hotspot because of the advantages of high thermal storage density, high thermal conductivity, moderate phase change temperature, and low price. However, some problems have restricted the application of salt hydrate heat storage materials, such as phase separation, supercooling, and corrosion of the metal container. A microencapsulated PCM using the microencapsulated technology of solid PCM coated packaging with core-shell structure composite material is an effective method to solve the above problems. In this paper, the research situations involving microencapsulated salt hydrate are analysed. This review introduces the selection of core and shell materials, compares the different preparation methods of encapsulated salt hydrate PCMs and summarizes the application fields.

Keywords: salt hydrate, core-shell microcapsules, phase change materials, encapsulating methods, application

1. Introduction

With the rapid development of global industry, a great deal of energy is consumed. At the same time, the increase in energy demand has spurred people to find more effective energy technologies to achieve rational utilization of energy structures in the global economy (Waqas A. and Ud Din Z., 2013). The development of renewable energy must be accelerated, such as solar energy, wind energy, water energy, and so on (Milian Y.E. et al., 2017; Xu B. et al., 2015; Mellioulis S. et al., 2015). However, these energy sources are constrained by their own characteristics for large-scale development. For example, because of changes in time and season, solar energy and wind energy are discontinuous and unstable (Tyagi V.V. et al., 2016). Affected by environmental, ecological, and safety issues, the development of hydropower and nuclear energy has also been limited. Thermal energy storage has been developed in the past decades, as it can transfer heat to storage during the charging, and release it during the discharging. Thermal energy storage has two methods usually, including sensible heat or latent heat. However sensible heat storage material has the lower storage capacity compared to the latent heat storage materials, which lead to the sensible heat storage systems need to occupy a huge volume and large space. Therefore, latent heat storage called phase change materials has a high storage density with a small temperature during storing and releasing heat (Zhang H.L. et al., 2016). Phase-change energy storage technology can realize multi-energy comprehensive application and allow safe, continuous, and stable output through the application of large-scale energy storage technology (Tyagi V.V. et al., 2012).

Phase change energy storage technology involves the energy storage and release of latent heat generated by phase change materials (PCMs) during the process of phase change, thereby alleviating the contradiction of the mismatch between the supply of heat energy and the demand in time and space (Farid M.M. et al., 2004; Pasupathy A. et al., 2008), which is the key technology to achieve energy conservation and comprehensive gradient utilization. Energy storage is directly affected by the performance of PCMs. The primary selection criteria of PCMs include high thermal storage capacity, high thermal conductivity, safety and low price. The PCMs are mainly classified by chemical composition, including organic...
PCMs (paraffin, fatty acids, etc.) and inorganic PCMs such as salt hydrates, and others (Zalba B. et al., 2003; Zhou D. et al., 2012; Su W. et al., 2015). Their classification and corresponding characteristics are shown in Fig. 1. Compared with organic PCMs, inorganic PCMs have the advantages of high heat storage density, high latent heat during the phase change process, and high thermal conductivity. Salt hydrates are typical inorganic PCMs and have outstanding advantages such as low prices and the fact that they are easy to obtain. Therefore, salt hydrate PCMs have the economic and technical feasibility and broad application prospects in many fields, such as solar energy utilization (Xiao X. et al., 2013), building energy conservation (Khudhair A.M. and Farid M.M., 2004; Su J.F. and Wang S.B., 2012), power system peak shaving, waste heat recovery, and so on (Hyun D.C. et al., 2014; Lecompte T. et al., 2015).

However, salt hydrate PCMs have problems such as phase separation, supercooling, leakage, and instability during phase change process (Zhang Y. et al., 2018), which limits their large-scale application in many fields (Cao L. et al., 2014; Song S. et al., 2014). The microencapsulation technique is an effective method for salt hydrate, as it can solve the leakage problem, increase the heat transfer area, reduce the reaction with the external environment and control the volume change during phase change process. (Fang G.Y. et al., 2010; Jamekhoshid A. et al., 2014; Su W. et al., 2015; Liu C.Z. et al., 2015).

Generally, microencapsulated PCMs refer to the core-shell PCMs. Occasionally, some researchers deemed that the shape-stabilized PCMs also belongs to the microencapsulated PCMs category (Zhao C.Y. and Zhang G.H., 2011). The shape-stabilized PCMs are mostly integrated PCMs with porous materials by capillarity (Milian Y.E. et al., 2017), which could solved the problems of salt hydrate PCMs mentioned above. However, when the temperature increases and reaches the phase change point, the liquid PCMs will slowly leak out from the micropores, which results the cycle performance of shape-stabilized PCMs decrease at high temperature. In comparison, the core-shell microencapsulated PCMs are solid or liquid PCM particles with a core-shell structure coated by film-forming material, thereby overcoming the shortcomings of the shape-stabilized PCMs and improving the performance of PCMs (Milian Y.E. et al., 2017; Zhao C.Y. and Zhang G.H., 2011). The structure of a core-shell microencapsulated PCM consists of core material and a shell material wrapped around the core. The core material can be either a PCM or a plurality of PCMs or the mixture with stabilizers, diluents and excipients. Shell materials are mostly made of stable, soft, and odorless polymer materials. The polymer material must be able to form a film on the surface of the core material, and has no reaction with the core material, being chemically compatible (Liu H. et al., 2019).

2. Selection of core and shell materials

2.1 Core materials

The core material is the phase change material. The principles of selection are large latent heat of phase change, a suitable phase change temperature, good
stability and durability, low likelihood of leaking, large thermal conductivity, reversibility in a phase transition, and good chemical compatibility (Milian Y.E. et al., 2017). The phase change is reversible, and the chemical compatibility is good (Zhang J. et al., 2011). Salt hydrate PCMs are increasingly favored for their outstanding advantages such as high latent heat and low cost. Salt hydrates, as shown in Table 1, are typical of the most studied PCMs. Although there are many salt hydrates, at present, the successfully coated salt hydrates as the core materials are Na2SO4·10H2O, CaCl2·6H2O, Na2HPO4·12H2O, Mg(NO3)2·6H2O, Na2CO3·10H2O, and so on (Sharma S.D. et al., 2004; Sharma A. et al., 2009; Cabeza L.F. et al., 2011; Su W. et al., 2015; Yang J.M. and Kim J.S., 2017). The thermal properties of the microencapsulated PCMs are shown in Table 2.

**2.2 Shell materials**

From the viewpoint of structure stability, the shell material should meet the characteristics of high strength, high toughness, good compactness and good chemical stability to maintain its integrity and avoid leakage of core material under the action of external force. Considering the preparation and use of the material, the shell material should have good chemical compatibility with the core material, no corrosion, no penetration, and it should be cheap and easy to obtain. In addition, to maintain the structure stability of core-shell microencapsulated PCMs, the melting point of the shell material should be higher than both the phase transition temperature of the core material and the highest temperature to be used.

Commonly shell materials are divided into organic and inorganic materials. From the literatures, most of the published papers are reported on the preparation of core-shell microencapsulated PCMs with organic shell materials, which means organic materials are easier to form core-shell microencapsulated PCMs (Liu H. et al., 2019). Generally used organic shell materials for coating salt hydrates are urea-formaldehyde resin, polymethyl methacrylate, styrene, polyurethane, and ethyl 2-cyanoacrylate, as shown in Table 2. Organic shell materials are costly and contain many harmful substances, such as benzene and aldehyde. Therefore, inorganic shell materials are more preferable due to the high thermal conductivity, safety and low prices. Although most of the inorganic shell materials have poor structure stability, considering the advantages of the inorganic shell materials, the development of new inorganic shell materials is important for improving the performance of shell materials and promoting the application and development of salt hydrate encapsulated PCMs.

**3. Methods for preparation of salt hydrate core-shell phase change materials**

The encapsulation methods of phase change core-shell PCMs are divided into chemical method and physical method (Su W. et al., 2015; Košny J., 2015; Liu H. et al., 2019), and their classification characteristics are shown in Table 3. Among them, the suspension polymerization method, the complex coacervation method and the spray
drying method are not suitable for the encapsulation preparation of inorganic PCMs due to their solubility and system stability problems. According to the literature research, the preparation methods of salt hydrate core-shell microcapsules mainly include in-situ polymerization method, solvent evaporation method and a few other methods such as sol-gel method and interfacial polymerization method. The specific preparation process is also shown in Table 4.

| Table 2 Thermal properties of hydrate salt core-shell microcapsules. |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| PCMs             | $T_m/°C$         | $\Delta H_m/J\cdot g^{-1}$ | Shell Size       | $T_c-s/°C$       | $\Delta H_{c-s}/J\cdot g^{-1}$ | Ref.             |
| Mixtures (PEG1000/Na$_2$CO$_3$·10H$_2$O/n-alkanes) | 38.6             | 235.2             | Urea Resin       | 1–500 μm         | 17.7/15.8          | 44.6/42.5         | (Sarier N. and Onder E., 2007) |
| Na$_2$SO$_4$·10H$_2$O | 27.9             | 254.0             | SiO$_2$          | 100 nm           | —                 | 180.7            | (Zhang J. et al., 2011) |
| Na$_2$CO$_3$·10H$_2$O Na$_2$CO$_3$·10H$_2$O | 38.6             | 235.2             | TMPTA and MS     | 1.5 mm           | 28                | 100              | (Platte D. et al., 2013) |
| Na$_2$HPO$_4$·12H$_2$O | —                 | —                 | TMPTA and MS     | —                | 24                | 200              | (Platte D. et al., 2013) |
| Mg(NO$_3$)$_2$·6H$_2$O | 93/74            | 160.2             | Ethyl-2-cyanoacrylate | 100–200 nm     | 91/83             | 83.2             | (Graham M. et al., 2016) |
| MgSO$_4$·7H$_2$O | 50.59            | 69.83             | Urea Resin       | 35 μm            | 48.36             | 25.46            | (Liu C.Z. et al., 2017a) |
| Na$_2$HPO$_4$·7H$_2$O | 49.9             | 218.93            | SiO$_2$          | —                | 47.23             | 199.47 (Max)     | (Liu C.Z. et al., 2017b) |
| Na$_2$HPO$_4$·12H$_2$O | 34.5             | 265.0             | Cellulose acetate butyrate and diphenylmethylenediisocyanate | 3 μm           | 26.69             | 140.4            | (Salaün F. et al., 2010) |
| Na$_2$HPO$_4$·12H$_2$O | 34.72            | —                 | Urea Resin       | 500 nm           | 41.5              | 121.2            | (Wang T.Y. et al., 2013) |
| Na$_2$HPO$_4$·7H$_2$O | 34.7             | 177.8             | Poly MMA with EA | 6.8 μm           | 51                | 145.5            | (Huang J. et al., 2013) |

| Table 3 Preparation methods and properties of nano/microencapsulated phase change materials. |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Methods          | Scale/μm         | Advantages       | Disadvantages    |
| Chemical Processes contain in-situ, interfacial polymerization, emulsion and suspension polymerization |
| In-situ          | 0.05~1100        | Easy to operate  | Hard to control and easy to reunite. |
| Interfacial polymerization | 0.5~1000       | Good compactness for shell and high reaction speed | Limited options for a salt hydrate system. |
| Emulsion         | 0.05~5           | Good cooling, do not use volatile solvents and low viscosity | — |
| Suspension polymerization | 2~4000       | High coating rate, small particle size and pollution. | — |
| Physical Processes contain sol-gel process, coacervation, solvent evaporation and spray-drying |
| Sol-gel process  | 0.2~20           | Mild reaction condition and homogeneous phase distribution | — |
| Coacervation     | 2~1200           | Controllable diameter and large pH range | No large-scale production |
| Solvent evaporation | 0.5~1000     | Low price and easy operation | No large-scale production and long cycle |
| Spray-drying     | 5~5000           | Low cost and mass production | Easy to reunite at high temperature. |
3.1 In-situ polymerization method

When the core-shell PCMs are prepared through in situ polymerization method, it involves a process whereby the reaction monomer and catalyst are added into the dispersion medium, and the core material is the dispersed phase. The monomer undergoes prepolymerization at the beginning of the reaction, and then the prepolymer is polymerized. When the prepolymer polymerization size is gradually increased, it is deposited on the surface of the core material. Because of the continuous progress of crosslinking and polymerization, the microencapsulated shell of the core material is finally formed (Zhao C.Y. and Zhang G.H., 2011). Fig. 2 shows the process of encapsulations of n-octadecane with resorcinol-modified melamine-formaldehyde shell using the in situ polymerization method (Zhang H. and Wang X., 2009a).

Sarier N. and Onder E. (2007) used urea-formaldehyde resin as the shell to encapsulate Na₂CO₃·10H₂O and n-hexadecane. Polyethylene glycol 1000 was used as the dispersant. The prepared capsule has a smooth surface and no leakage. It is suitable for textile products.

Zhang J. et al. (2011) used SiO₂ as a shell to encapsulate Na₂SO₄·10H₂O as a core material in situ polymerization method. The results indicate the microcapsules can improve the supercooling and phase segregation of the pure salt hydrate.

### Table 4 Preparation of salt hydrate core-shell microcapsules.

<table>
<thead>
<tr>
<th>Capsules scale</th>
<th>Core materials</th>
<th>Shell materials</th>
<th>Emulsifiers</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano (100 nm)</td>
<td>Na₂SO₄·10H₂O</td>
<td>TEOS and 3-aminopropyltriethoxysilane</td>
<td>SDS and n-pentanol</td>
<td>(Zhang J. et al., 2011)</td>
</tr>
<tr>
<td>Nano (100–200 nm)</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>Ethyl-2-cyanoacrylate</td>
<td>Tween 80 and Span 20</td>
<td>(Graham M., 2016)</td>
</tr>
<tr>
<td>—</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>Ethyl-2-cyanoacrylate</td>
<td>Tween 80 and Span 20</td>
<td>(Graham M. et al., 2017)</td>
</tr>
<tr>
<td>—</td>
<td>Na₂SO₄·10H₂O</td>
<td>Ethyl-2-cyanoacrylate</td>
<td>Tween 80 and Span 20</td>
<td></td>
</tr>
<tr>
<td>Micro (35 μm)</td>
<td>MgSO₄·7H₂O</td>
<td>Urea Resin</td>
<td>SDBS</td>
<td>(Liu C.Z. et al., 2017a)</td>
</tr>
</tbody>
</table>

### Fig. 2 Fabrication of microencapsulated PCM by in-situ polymerization. Reprinted with permission from Ref. (Zhang H. and Wang X., 2009a). Copyright: (2009a) Elsevier B.V.
Na₂SO₄·10H₂O and have good cycling performance after 60 times, and good performance.

Platte D. et al. (2013) prepared salt hydrate microcapsules by in-situ polymerization of mercaptan Michael addition using TMPTA and polyether as shells and Na₂CO₃·10H₂O, Na₂CO₃·10H₂O and Na₂HPO₄·12H₂O as core materials.

Wang T. et al. (2013) selected Na₂HPO₄·12H₂O as the core material and urea-formaldehyde resin as the shell material. The microcapsules were successfully prepared by in-situ polymerization. The effects of the molar ratio of urea and formaldehyde on the structure and morphology of the obtained microcapsules were studied. The results show that the prepared microcapsules have a core-shell structure with a well-proportioned coating. Its average particle size was about 500 nm, the latent heat of phase change was 121.2 J·g⁻¹, and the weight loss was less than 10 % in the temperature range of 30–84 °C.

Graham M. et al. (2016) used in-situ microemulsion polymerization method to prepare microcapsules with 2-ethyl cyanoacrylate polymer as shell material and Mg(NO₃)₂·6H₂O as core material. The capsule size was 100–200 nm. The latent heat of the PCM was reduced by 3 % after 100 times of phase thermal cycles, and the degree of supercooling was greatly reduced. This was the first time to produce a longer life (100 times) for salt hydrate microcapsules. The latent heat of the microcapsule was 83.2 J·g⁻¹. After hundreds of thermal cycles, the latent heat value did not change much. The researchers also confirmed by Fourier transform infrared spectroscopy and observation that the chemical properties of the microcapsules were very stable after hundreds of thermal cycles. Graham M. et al. (2017) successfully prepared microcapsules containing Mg(NO₃)₂·6H₂O, Na₂HPO₄·12H₂O and their mixture as core materials by the above methods.

Liu C.Z. et al. (2017a) successfully prepared microcapsule by in-situ emulsion polymerization with urea formaldehyde resin (UR) as the shell material and MgSO₄·7H₂O as the core material. They analysed the microscopic morphology, particle size distribution, phase change temperature, phase change latent heat of microcapsules. The results reveal that when using sodium dodecyl benzene sulfonate as the emulsifier, and emulsifier content was 0.5 g, the microcapsules had a smooth, uniform particle size; the average diameter was 34.99 microns, the phase change temperature of microcapsule was 48.36 °C and the phase change latent heat was 25.46 kJ·kg⁻¹.

### 3.2 Solvent evaporation method

The solvent evaporation method means that the shell material or the shell material formed by the reaction is dissolved in the continuous phase first, and after the dispersion medium is volatilized, a shell is formed on the surface of the droplet to obtain a microcapsule structure (Salaün F. et al., 2010). Fig. 3 shows a process by an interfacial polymerization.

Salaün F. et al. (2010) used a solvent evaporation method, cellulose acetate butyrate and diphenylmethylene diisocyanate as shell materials, and Na₂HPO₄·12H₂O as core material to prepare phase change microcapsules. The author discussed the effects of different solvents such as acetone, toluene, carbon tetrachloride, and chloroform on the morphology and coating rate of microcapsules, using toluene and chloroform as organic solvents to generate Na₂HPO₄·12H₂O@polyurethane microcapsules with a coating rate of 68.4 % and a uniform particle size distribution. Through SEM observation, the morphology of the microcapsules was strongly influenced by the solvent. The thermal properties of the microcapsules were studied by TGA and DSC analysis, and the results show that the thermal properties of the microcapsule depended on the content of the core material and the synthesis conditions.

Wang T.Y. and Huang J. (2013) used polymethyl methacrylate (PMMA) as a shell material to encapsulate Na₂HPO₄·12H₂O using the same method. The polymerization was sufficiently carried out at a reaction temperature of 80 to 90 °C for 4 hours to form a composite phase change microcapsule with a radius of 1–10 μm. The

![Fig. 3 Steps of microencapsulation by solvent evaporation. Reprinted with permission from Ref. (Li M. et al., 2008). Copyright: (2008) Elsevier B.V.](image-url)
literature indicates that it can reach a maximum phase change enthalpy of 173.9 kJ/kg at a temperature of 51 °C.

To lessen the brittleness of polymethyl methacrylate shell material and improve the processing property of salt hydrate microcapsules, Huang J. et al. (2013) studied Na₂HPO₄·12H₂O encapsulation by solvent evaporation method with shell material made of methyl methacrylate and ethyl acetate. Microencapsulated PCMs with a phase change temperature of about 51 °C and a phase change enthalpy of 150 J·g⁻¹ were prepared. The reason for the change in phase change temperature was analysed based on the characterization data, which were due to the uneven distribution of components and the loss of the water component during the preparation process. Thus, the core material coated with the microcapsules was actually Na₂HPO₄·7H₂O.

Wang T. et al. (2013) encapsulated DSP using PMMA and UF at 51.51 and 41.15 °C with the corresponding latent heat of 142.9 and 121.20 kJ·kg⁻¹. The results show that they achieved encapsulation efficiencies were only 55.74 % and 63.97 % respectively. The organic solvent caused leakage after a few multiple heating-cooling cycles.

3.3 Interfacial polymerization method

The interfacial polymerization method refers to emulsifying or dispersing a core material in a continuous phase in which a shell material is dissolved, and then the monomer forms the microcapsule on the surface of the core material by polymerization. The interfacial polymerization can be mainly divided into interface addition polymerization and interface condensation polymerization method, which is suitable for preparing microcapsules of water-soluble core material (Sarier N. and Onder E., 2012). Fig. 4 shows a process by Zhang H. and Wang X. (2009b) in interfacial polymerization.

Hessbrugge B.J. and Vaidya A.M. (1997) prepared Na₂HPO₄ as the core material and polyamide as the shell material to prepare microcapsules by interfacial polycondensation. The results indicate that the microcapsules are 0.5 to 2.5 mm in size and can be used as a buffer.

3.4 Sol-gel method

The sol-gel process contains three steps: First, the precursor is mixed uniformly with the solvent. After the hydrolysis condensation chemical reaction, a stable dispersion of colloidal particles is generated. Last, a gel with a three-dimensional network structure was formed after aging of the sol (Macwan D.P. et al., 2011). Fig. 5 shows the process of the sol-gel method.

Liu C.Z. et al. (2017b) successfully prepared Na₂S₂O₃·5H₂O@silica phase change microcapsules by sol-gel method, using silica as the shell material and sodium thiosulfate pentahydrate as the core material. They measured the microstructure, particle size distribution, phase change temperature and latent heat of phase change microcapsules. They analysed the effects of different emulsifier content and the mass ratio of core material to shell material. The results show that the phase change microcapsules had the regular spherical structure, smooth and compact surface when the mass ratio of the core material and the shell material and emulsifier is 1:0.4:0.04 and that

![Fig. 4](image-url) Microcapsule manufactured by interfacial polycondensation. Reprinted with permission from Ref. (Zhang H. and Wang X., 2009b). Copyright: (2009b) Elsevier B.V.
The particle size distribution was uniform. The latent heat of the prepared phase change microcapsules was 199.47 kJ·kg⁻¹, and the coating rate was 94.65%. After the silica coating, the supercooling degree and thermal conductivity were improved, and the thermal stability was obviously improved. At the same time, the leakage caused by the flow of the core material after melting was solved, thus extending the cycle life of the inorganic salt hydrates in practical application.

Yang J.M. and Kim J.S. (2018) successfully prepared microcapsules by using a combination of sol-gel and interfacial polymerization with siloxane and polyurea as shell materials and CaCl₂·6H₂O as core material. They studied the characteristics of microcapsules with different core-shell ratios and different pH values. The results indicate that the microcapsules can be prepared when the core-shell mass ratio was 3.0, and when the pH was between 1.5 and 2.8. Especially when the pH was 2.35 and 2.55, the surface of the microcapsule was smooth with excellent thermal properties and a high coverage ratio.

3.5 Comparison of different microencapsulation methods

The review has shown that salt hydrate PCMs can be encapsulated by different methods such as in-situ polymerization, interfacial polymerization, solvent evaporation, sol-gel methods, and so on. In brief, in-situ polymerization can be suitable for producing nanocapsules, but it is difficult to achieve large-scale production because a high stirring rate is needed to generate droplets during the encapsulation process, which will consume a great deal of energy and produce high costs. Solvent evaporation can be encapsulated using organic shells successfully. However, the organic shells have poor thermal conductivity and the preparation process is not controllable. Few studies have been conducted on interfacial polymerization and sol-gel methods for salt hydrate core-shell microencapsulation.

4. Application

4.1 Temperature-regulating fabric

As early as the 1980s, NASA carried out research on the application of microencapsulated PCMs in thermal-regulation protective clothing. Since then, much-applied research has been carried out in the field of clothing (Giraud S. et al., 2005; Giraud S. et al., 2002). This type of functional clothing can adjust the temperature of the clothing and its surroundings, reduce the difference in skin temperature, and make the clothing more comfortable. In the main process, microcapsules are added to the fibre or coated on the surface of cotton cloth to develop fibre and cloth with self-regulating temperature performance. Sarier N. and Onder E. (2007) accomplished the microencapsulation of PCMs by a manufacturing technique that can ultimately be used in different textile applications.

4.2 Buildings

PCMs have been used in buildings to meet comfort thermal requirements for peoples (Hawes D.W. et al., 1993; Neeper D.A., 2000; Kumirai T. et al., 2019). But, there are some problems for PCMs in building applications, such as interaction between building structure and...
PCMs. Leaks of PCMs to decrease the lifetime of the structure and poor heat transfer for PCMs in the solid state. To overcome the above problems, salt hydrate core-shell PCMs are applied in the field of energy-saving building materials. Physical methods such as miscibility and filling can be combined with traditional building materials to prepare energy-saving building materials such as plates, coatings, and bricks with the function of phase change energy storage. A comprehensive review of encapsulation techniques for inorganic phase change materials and the influence on their thermophysical properties had been carried out by Milian Y.E. et al. (2017). In this review, the researcher made a detailed summary of the application trend of microcapsules in the field of buildings. The application of microcapsule phase change energy storage materials in the buildings can reduce the fluctuation of indoor temperature and the power consumption of refrigeration or heating equipment to achieve the purpose of energy savings. But the researchers still admit great challenges to enlarge thermal and cycling stability and reduce corrosion with building materials (Ma Z. et al., 2016).

Farid M.M. et al. (2004) mixed calcium chloride microcapsules in hexahydrate into building cement and obtained a good temperature control effect. In addition, salt hydrate microcapsule PCMs can also be used for cooling electronic components (Wirtz R.A. et al., 2012; Kandasamy R. et al., 2008), waste heat recovery, aerospace applications and so on.

5. Conclusions

This review introduced the selection of core and shell materials, compared the different preparation methods of encapsulated salt hydrate PCMs and summarized the application fields. Four types of preparation to successfully prepare salt hydrate core-shell microencapsulation were introduced: the in-situ polymerization method, solvent evaporation method, interfacial polymerization method and sol-gel method. The research works on encapsulated salt hydrate core-shell PCMs are relatively few compared to those on organic core-shell microencapsulation. The research has mainly focused on the study of the preparation methods, mostly using polymers as shell materials because a polymer with a low coefficient of thermal conductivity will affect the heat transfer performance of microcapsule PCMs, a new type of inorganic shell materials must be developed. Encapsulated salt hydrate core-shell PCMs have not been applied at large scales yet, but these PCMs have great potential application value. Therefore, it is necessary to strengthen the research on preparation technology and actively expand its application fields.

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Nomenclature

DSP Disodium hydrogen phosphate dodecahydrate
EA Ethyl acrylate
MMA Methylmethacrylate
PCMs Phase change materials
PMMA Polymethyl methacrylate
SDBS Sodium dodecyl benzene sulfonate
SDS Sodium dodecyl sulfonate
TEOS Tetraethyl orthosilicate
TMPTA Trimethylol propane triacrylate
UF Urea-formaldehyde resin

References

Giraud S., Bourbigota S., Rocherya M., Vromana I., Tighzertb L., Delobele R., Microencapsulation of phosphate: Applica-


Milian Y.E., Gutierrez A., Grageda M., Ushak S., A review on encapsulation techniques for inorganic phase change materials and the influence on their thermophysical properties, Renewable & Sustainable Energy Reviews, 73 (2017) 983–999


Sarier N., Onder E., The manufacture of microencapsulated...
Song S., Dong L., Qu Z., Ren J., Xiong C., Microencapsulated phase change materials suitable for the design of thermally enhanced fabrics, Thermochimica Acta, 452 (2007) 149–160. DOI: 10.1016/j.tca.2006.08.002


Sharma S.D., Kitano H., Sagara K., Phase change materials for low temperature solar thermal applications, Research Reports of the Faculty of Engineering, Mie University, 29 (2004) 31–64.

Song S., Dong L., Qu Z., Ren J., Xiong C., Microencapsulated capric–stearic acid with silica shell as a novel phase change material for thermal energy storage, Applied Thermal Engineering, 70 (2014) 546–551. DOI: 10.1016/j.applthermaleng.2014.05.067


Tyagi V.V., Buddhi D., Kothari R., Tyagi S.K., Phase change material (PCM) based thermal management system for cool energy storage application in building: An experimental study, Energy and Buildings, 51 (2012) 248–254. DOI: 10.1016/j.enbuild.2012.05.023


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