Optimization of preparation and analysis of Paraffin/SiO₂ composite PCMs via sol-gel method

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Abstract: Using the economical and environmental paraffin as core, Paraffin/SiO₂ composite phase change materials (PCMs) were prepared by sol-gel method. Industrial water glass for preparation of the nano-SiO₂ was served as a shell with the modification of silane coupling agent. We combined Soxhlet extraction with penetration circle for the coating rate and the optimization of preparation was obtained via SPSS. The composite PCMs were investigated by SEM, TG, FT-IR, DSC technique. The results indicated that the optimization of preparation (PH=4.5 and T=35℃) was available. When the efficient coating rate of paraffin reached up to 60.04%, the phase-transition temperature was 38.73℃ and the enthalpy of phase change was 72.88J/g. Moreover, thermal stability and reliability of the paraffin/SiO₂ composite PCMs were proved through TG curves. So it could be formulated that paraffin/SiO₂ composite PCMs with no leakage, excellent thermal storage capacity could be employed in energy conservation as a kind of thermal functional material.

1. Introduction

The phase change materials (PCMs), referring to an efficient, environmental materials, have been automatically absorbed and released latent heat to maintain a certain temperature. Experience has shown that it is practically possible to make high latent heat composite phase change materials which are preferably contributed to indoor temperature. In the last years, several candidates of PCMs (for example, salt, paraffin, metals, polyalcohol, alloys and fatty acids[1-4]) for latent heat storage have been reported in several reviews[5-6], and applied successfully in solar energy storage, waste heat utilization, air-conditioning, building energy conservation and renewable energy application [7]. To improve recycling utilization of latent heat and reduce costs for building application, polymer such as polyethylene (PE) have been explored as a sealant to reduce paraffin seepage [8–10]. As follow up, it’s also noted that studies processing and quantifying PCM leakage were lacking [14]. Fang Chen and Michael Wolcott investigated the blends of paraffin with HDPE, LDPE, LLDPE and indicated that the leakage rate from HDPE is considerably slower than blends produced with LDPE or LLDPE for 66-h test in oven at 60℃. However, the existing skeletal materials such as polymer (e.g. PE, PMMA, resin, polyacrylate, polyving alcohool, etal.) were difficult to prepare for toxicity, flammability, low thermal conductivity and complex process conditions via situ polymerization and bulk polymerization. In order to solve the problems, much attention focused on inorganic shell (SiO₂) source of Methyl Orthosilicate (TEOS) [11-14]. Nevertheless, TEOS was high priced and poisonous so that it is difficult
to realize the marketization and popularization in the heat storage application field. Among the reported PCMs and composites, paraffin has been widely used as storage energy matter due to its higher heat enthalpy, self-nucleating ability, phase change temperature range, thermal and chemical stability, commercial availability and low cost. Owing to the above mentioned advantages, paraffin was very widely used in preparation of composite PCMs. Meanwhile, industrial water glass displaced TEOS as the silica source by sol-gel method. Hence, the objective of this paper is to fabricate a new kind of composite PCMs consisting of silicon dioxide (obtained from water glass) as the shell material and paraffin as the thermal energy storage medium. Optimization of preparation of paraffin/SiO\textsubscript{2} composite PCMs should be also researched.

2. Material and Methods

2.1 Materials

ParaffinC\textsubscript{n}H\textsubscript{2n+2}(No.33), as listed in Tab.1 and Tab.2, produced in Shenyang was applied for the phase change core. Sodium dodecyl benzene sulfonate (C\textsubscript{18}H\textsubscript{29}NaO\textsubscript{3}S, SDBS, AR), which was anionic surfactants having excellent emulsifying properties used as emulsifiers in this experiment, was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Water glass provided by Dalian Qinan Chemical Company was used as the source of silica via sol-gel method. Amberlite kation exchange resin supplied by Shanghai Huizhu Amberlite Company was used for ion exchange for the water glass. Silane coupling agent (KH-570) supplied by Nanjing Nengde Chemical Reagent Company was used as the surfactant in the sol-gel process. Aqueous ammonia n-hex ane as extraction agent and absolute ethyl alcohol was purchased from Sinopharm Chemical Reagent Company.

Table 1. Desirable characteristics of paraffin used as core.

| Characteristics | \( \rho \)g/ml | \( \Delta V \) % | \( \sigma \) w·m\textsuperscript{-1}·k\textsuperscript{-1} | \( T \) \( ^\circ \)C | \( \Delta H \) J/g |
|-----------------|--------------|----------------|-------------------|----------------|--------------|
| Paraffin        | 0.810        | 9.85           | 0.19              | 39             | 174.85       |

Table 2. Characteristic temperature on storage-release heat curves of different quality of paraffin.

| Mass of paraffin g | Starting time of storage heat min | The difference between the two beakers in stable conditions \( ^\circ \)C |
|--------------------|----------------------------------|-------------------------------------------------|
| 5                  | 24                               | 14.7                                            |
| 10                 | 22                               | 19.0                                            |
| 20                 | 19                               | 25.5                                            |

Comment: The difference between the two beakers in stable conditions = the temperature of the specimens – the temperature of the referential sample.

2.2 Preparation of paraffin/SiO\textsubscript{2} composite PCMs

The whole procedure included SiO\textsubscript{2} hydrogel prefabrication and the paraffin/SiO\textsubscript{2} composite PCMs preparation.

A. Preparation of SiO\textsubscript{2} hydrogel

Via sol-gel method, industrial water glass as raw materials were diluted with a certain amount of distilled water, \( V \) (water glass):\( V \) (distilled water) = 1:4, and stirred well. The mixed solution should be poured into cylindrical glass vessel which was full of amberlite kation exchange resin presenting strongly acid, consequently, the silicate solution (PH = 2-3) were obtained. The PH of silicate solution was adjusted with 1mol/L of NH\textsubscript{3}·H\textsubscript{2}O solution.

B. The different factors and levels of preparation process of composite PCMs
We should know the general belief that the more positive the coating rate of paraffin, the better performance of temperature adjusting. By investigating the different factors and levels on the influence of the optimum coating rate, we designed orthogonal experimental shown in Tab.3, as PH, temperature (T), paraffin/water ratio (P/W), paraffin/hydrated silica ratio (P/S).

Table 3. Experiment Scheme of composite PCMs.

| No. | PH | T℃ | P/W | P/S | coating rate% | Penetration circle% | efficientcoating rate% |
|-----|----|-----|-----|-----|---------------|---------------------|-----------------------|
| 1   | 3  | 25  | 1:1 | 1:1 | 68.18         | 57.98               | 10.2                  |
| 2   | 4  | 35  | 1:1 | 1:2 | 79.73         | 59.24               | 20.49                 |
| 3   | 4.5| 45  | 1:1 | 3:4 | 69.79         | 29.64               | 40.15                 |

A given mass of paraffin in a flask of 250ml with amount of SDBS in a water-bath at a required temperature were stirred rapidly about 2000r/min, as a consequence, the paraffin solution could generate large quantities of tiny emulsion drops. Then prepared SiO₂ hydrogel was slowly added into flask, stirring at low speed and mixing with emulsion. The silicate solution in the weak acid ambient experience dehydration polycondensation and the Si-O bonds connect with each other forming the three dimensional networks which provides the space for PCM molecular. The paraffin/SiO₂ composite PCMs were tentatively gained. In the aging procedure, the gaps in the gel shrink to be the pores along with the solvent volatilization and the tiny emulsion drops of paraffin left and disperse well in the porous structure so as to be immobilized in the Si-O network porous structure. However, the mixture should be remaining at the constant temperature, sucking out the excess liquid. Meanwhile, Ethyl alcohol was added to accelerate aging of mixed silicate solution. After the stiffening of silicate, the reaction mixture was put into a drying oven at 60℃ for 8 hours and then washed by hydrochloric acid and absolute ethyl alcohol alternately. The paraffin/SiO₂ composite PCMs were obtained after dried in the 80℃ drying oven.

2.3 Characterization of paraffin/SiO₂ composite PCMs
The coating rate was searched combining Soxhlet extraction with penetration circle. Morphology observations on the SiO₂ and the prepared composite PCMs were acquired by applying TEM (Tecnai G2 Spirit (FEI Co.)) and SEM (QUANTA 450). FT-IR (Nicolet 3600) analysis was used to determine the chemical component and compatibility of the composite PCMs. Thermal properties, including phase change temperature and latent heat of the specimens (including paraffin and paraffin/SiO₂ composite PCMs before and after thermal cycling test) were measured using DSC technique on a Mettler DSC822e instrument. The experimental measurements were carried out under a nitrogen atmosphere at a constant heating rate of 5℃/min. The heating temperature ranged from 5 to 80℃.Thermo-gravimetric analysis was used for examining the thermal stability and weight loss of the specimens on a Mettler TGA/SDTA851e thermo-analyzer. The samples were heated under a nitrogen atmosphere from atmospheric temperature to 500℃ at a heating rate of 10℃·min⁻¹.

3. Result and discussion

3.1 Optimization of preparation of efficient coating rate
The coating rate and penetration circle were as under. And the percentage of efficient coating (shown as under) expressed as the difference between above two percentages. Furthermore, the larger were this value of penetration circle, the more seriously paraffin core leak out.

Table 4. Experiment Scheme of composite PCMs.

| No. | PH | T℃ | P/W | P/S | coating rate% | Penetration circle% | efficientcoating rate% |
|-----|----|-----|-----|-----|---------------|---------------------|-----------------------|
| 1   | 3  | 25  | 1:1 | 2:1 | 68.18         | 57.98               | 10.2                  |
| 2   | 4  | 35  | 1:1 | 1:2 | 79.73         | 59.24               | 20.49                 |
| 3   | 4.5| 45  | 1:1 | 3:4 | 69.79         | 29.64               | 40.15                 |
The coating rate minus penetration circle equals the efficient coating.

Relying on SPSS17.0, the dependent variable, the efficient coating rate, was rationally analyzed. The results demonstrated that the significant value was 0.047 for PH, 0.466 for temperature, 0.663 for paraffin/water ratio, 0.628 for paraffin/hydrated silica ratio. The significance order from big to small of the effects of each factor on PH, Temperature, Paraffin/hydrated Silica, Paraffin/Water ratio. The principal factor of paraffin/SiO2 composite PCMs prepared by sol-gel method was relatively PH. Temperature, paraffin/water ratio and paraffin/hydrated silica ratio responding to the efficient coating rate had no significant effect.

Estimated marginal means in which Means, Standard Error and 95% Confidence Interval were present were shown as below (Dependent Variable: efficient coating rate). Fig.1 indicated that with the increase of PH, the efficient coating rate went up gradually. The increase in silicate polycondensation caused by variation of PH fast, and the viscosity of uniform mixture became greater. In that case, the internal free hydroxyl had no enough time to react. It therefore significantly led to more capillary cavities, where more paraffin could be absorbed. However, if excess PH was present in the SiO2 hydrogel, it would be possible that an amount of paraffin emulsion drops were rarely entered into the porous due to the silicate polycondensation reaction rapidly and closure of SiO2. Simultaneously, the faster the polycondensation react, the more difficult the experimental operation was.

![Figure 1. Estimated marginal means: PH.](image1)

![Figure 2. Estimated marginal means: temperature.](image2)

Figure 1. Estimated marginal means: PH. Figure 2. Estimated marginal means: temperature.

Adjusting the PH of the mixture, in fact, was similar with a catalyster. Different PH resulting in different degree of crosslinking of Si(OH)4 polycondensation. This was because as if PH was too low, i.e., the excess H+ was present amount to acid catalysis, the one-dimensional chain structure with low crosslinking was obtained. Oppositely, when PH was excessive, equivalently base catalysis, a large number of particles of high crosslink degree of Si(OH)4 tended to be agglomerated and to gel quickly. Fig.1 shows the efficient coating rate was up to 49.095%, when PH was equal to 4.5.
The preparation of paraffin emulsion needs a certain temperature and rotating speed, in that case, the enough shear force could be greater than vector sum between surface tension in the paraffin liquid drops and internal adhesion. The drops cracked and scaled down correspondingly. When the stable emulsion drops were mixed with hydrated silica prepared in normal temperature, excessive difference in temperature of two-phase should be responsible for phase separation, even stratification. Fig.2 shows the impact on efficient coating rate. As the temperature was at 35℃, the efficient coating rate was optimal value (34.273%). It’s well understood the effect of P/W on efficient coating rate given in Fig. 3. With increasing of P/W ratio, it indicated that the rate of paraffin wax by weight of emulsion was large. The viscosity was uniformly strong, and as consequence, the internal bonding stress was good. The paraffin emulsion with high stability could be formed under the same stirring speed and temperature. Whereas, P/W ratio was descended to 1, there was a bit of paraffin in emulsion, forming Water/Oil system difficulty, and less paraffin were capsulated in water membrane. The latent heat of composite PCMs was lower accordingly.

The P/S ratio influence appeared resemblance to P/W ratio, belonging to the category of materials proportion. The amount of paraffin core was directly reflected in the relative content of the composite PCMs. Therefore, under certain conditions, the more initial dosage, the greater the content of paraffin in the composite PCMs.

It was shown in Fig.4 with the increase of P/S, the percentage of paraffin mass increased and the content of silica in the wall was reduced correspondingly, the efficient coating rate also increased, however, it did not develop continuously. During the experiment, it was found that when P/S reached a certain value, the percent of penetration circle increased, resulting in an excess of PCM core not being fixed. Due to the finite capacity of the three dimensional networks which provides the space for PCM molecular, phase-paraffin core were leaked out to be not packed by the SiO2 networks.

![Figure 3](image1.png)  
Figure 3. Estimated marginal means: P/W.  
![Figure 4](image2.png)  
Figure 4. Estimated marginal means: P/S.

Therefore, optimization of preparation (PH=4.5, T=35℃, paraffin/water ratio =0.25, paraffin/hydrated silica ratio=0.75) was available.

3.2 Morphology investigation of the paraffin/SiO2 composite PCMs

Morphologies of paraffin/SiO2 composite PCMs were investigated by TEM and SEM analysis and the images are shown in Fig.5 and Fig.6, respectively. Fig.1 demonstrated the three dimensional networks formed by sol-gel performed skeleton, and composite PCMs were assumed solid phase at the macro level. As shown in Fig.6 (a), comparing to (b), paraffin/ SiO2 composite PCMs had a smooth surface, fuzzy interface, apparent densification. This means in Fig.6 (a), paraffin as phase change core had been saturated in the networks of SiO2, which was contributed to densification. In addition, Fig.6 (b) as under signified, morphology image verified strongly paraffin was extracted from composite PCMs after soxhlet extraction owing to sleek interface and a few of pores.

3.3 Chemical characterization of the paraffin/SiO2 composite PCMs

Fig.7 displays the FT-IR absorption spectra of paraffin, SiO2, paraffin/ SiO2 composite PCMs and the residue of PCMs. In the pure paraffin spectrum, the peaks at 2920 cm⁻¹, 2850 cm⁻¹ are C-H stretching peaks and the peaks at 1470 cm⁻¹ are -CH₂ bending peaks. The peaks at 720 cm⁻¹ correspond to rocking vibration and bending in plane for paraffin. In the spectrum of SiO₂, the peaks at 1000-1200
cm\(^{-1}\), 940 cm\(^{-1}\), 815 cm\(^{-1}\), 460 cm\(^{-1}\) represent Si-O-Si antisymmetric stretching vibration peaks, Si-OH absorption peaks, Si-O-Si symmetrical stretching vibration and O-Si-O bending peaks. Comparing FT-IR spectra of composite PCMs with that of paraffin and SiO\(_2\), it’s distinctly seen the FT-IR spectra of paraffin/ SiO\(_2\) composite PCMs comprises both the peaks of paraffin and SiO\(_2\). It was also said the spectra illustrated the composites were just a physical combination of silicate and paraffin. Meanwhile, in the spectrum of composite PCMs, the peaks at 1638 cm\(^{-1}\) and 1720 cm\(^{-1}\) were the most intensive absorption band representing the carbonyl group from silane coupling agent (KH570) [15]. The peak at the wave number of 1410-1300 cm\(^{-1}\) in the composite is also attributed to the vibrations of O-H in plane. The conclusion of FT-IR was obtained there were no new noticeable functional groups varied in the compound. That was said paraffin and SiO\(_2\) had excellent compatibility.

Theoretically, the residue of composite PCMs after Soxhlet extraction should be only SiO\(_2\). Then FT-IR of residue of composite PCMs and pure SiO\(_2\) was researched given in Fig.3 comparing with pure paraffin and SiO\(_2\). A conclusion assumed as another evidence of successful formation of composite PCMs, which was not simple blended, but formed covalent bond hybridization possessing a certain intermolecular forces attributing to cage effect.

3.4 Thermal properties analysis of the paraffin/SiO\(_2\) composite PCMs

Phase change temperature and latent heat are key performances which determine the thermal storage capacity contributing to indoor temperature in the thermal storage application. Phase change behaviors of pure paraffin and paraffin/SiO\(_2\) composite PCMs were evaluated by DSC, and the thermograms are displayed in Fig.8. As given in Fig.8, paraffin/SiO\(_2\) composite PCMs show a both endothermic peaks on the DSC heating thermogram. The phase change temperature of the composite PCMs was 13.7°C and 38.73°C, which was very close to that of the pure paraffin (14.68°C and 39.24°C). As the nano-SiO\(_2\) DSC thermogram indicated it rarely happened any heat change below the temperature of 300°C[16]. In other words, it means nano-SiO\(_2\) doesn’t play a role in the latent heat absorption of the composite PCMs below 50°C, therefore, the heat absorption peaks of the composite PCMs should be attributed to the melt of paraffin in the composite. However, the latent heat of the composite, for instance, No.7 was showed to be up to 65.2427 J/g. It’s because the penetration circle of the samples had a large area (59.24%), and some paraffin was not enclosed in the network of the SiO\(_2\) combining.
with Tab.4. The rest of results confirmed that paraffin had been packed in the nano-SiO₂ particles and the composite PCMs had an acceptable phase change temperature and latent heat value for building energy saving and energy storage.

3.5 Thermal stability and reliability of the paraffin/SiO₂ composite PCMs

Thermal stability and reliability tests were characterized by thermal decomposition stability. Thermal decomposition stability focuses on the behavior of PCMs at high temperatures to determine the weight loss in the service process. Fig.9 shows the TG measurement curves of paraffin, and paraffin/SiO₂ composite PCMs. As was shown, paraffin, whose initial temperature of the weight loss was about 150℃, decreased its weight in the temperature range of 200-300℃. The weight loss ratio almost reached 100 percent at the temperature of 300℃. The composite PCMs, by contrast, had an obvious weight loss in the temperature range of 200-300℃, which was matched to the weight loss of paraffin.

![Figure 7. FT-IR spectra of pure paraffin, SiO₂, paraffin/SiO₂ composite PCMs and residue of composite PCMs (a: Residue of No.15; b: Residue of No.7; a’: No.15; b’: No.7).](image)

However, the weight loss initial temperature of paraffin in the composite PCMs had been prolonged and the temperature range extended, which explains that the melt of paraffin in the composite PCMs is inhibited by SiO₂ in some degree. At 300℃, the paraffin was considered to be completely volatilized and the weight loss ratio of the composite PCMs was measured as 53.32% (No.7).

4. Conclusions

The composite PCMs were made from industrial water glass combined with paraffin. Based on paraffin as the phase change material and industrial water glass as the silica source, sol-gel method was used successfully to prepare the paraffin/SiO₂ composite PCMs. The TEM, SEM and FT-IR tests showed that the paraffin had been embedded into the network pores of nano-SiO₂. Meanwhile, there were no chemical reactions between the two constituents because of no functional groups. The optimization of preparation was PH=4.5, T=35℃. The latent heat of the paraffin/SiO₂ composite PCMs was 72.88J/g, and the phase change temperature was 38.73℃. TG and thermal cycling experiment results demonstrated the thermal stability and reliability of the composite PCMs. Overall, it could be considered as potential thermal energy storage material to keep the indoors comfortable and energy saving.
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