Optimized Preparation of Cetyl Alcohol-Palmitic Acid-Lauric Acid/SiO_2 Composite Phase-Change Humidity-Control Material (Postprint)

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Abstract

Using SiO2 as the carrier material and cetyl alcohol-palmitic acid-lauric acid as the phase change material, a cetyl alcohol-palmitic acid-lauric acid/SiO2 composite phase-change humidity-control material was prepared. The influence of various factors on the humidity-control and temperature-control performance of the composite material was investigated using uniform design and multivariate nonlinear regression methods. The results indicate that the order of factor influence on performance is as follows: molar ratio of anhydrous ethanol to tetraethyl orthosilicate, solution pH value, molar ratio of cetyl alcohol-palmitic acid-lauric acid to tetraethyl orthosilicate, ultrasonic power, and molar ratio of deionized water to tetraethyl orthosilicate. The optimal preparation parameters are: solution pH value of 2.68, ultrasonic power of 113 W, molar ratio of deionized water to tetraethyl orthosilicate of 9.03, molar ratio of anhydrous ethanol to tetraethyl orthosilicate of 5.22, and molar ratio of cetyl alcohol-palmitic acid-lauric acid to tetraethyl orthosilicate of 0.51.

Full Text

Optimization for Preparation of Phase Change and Humidity Control Composite Materials of Hexadecanol-Palmitic Acid-Lauric Acid/SiO2

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Abstract
Phase change and humidity control composite materials of hexadecanol-palmitic acid-lauric acid/SiO2 were prepared with SiO2 as carrier material and

hexadecanol-palmitic acid-lauric acid as phase change material. The effect of processing parameters on performance of humidity- and temperature-control of the composite materials was investigated by uniform design and multivariate nonlinear regression. The results show that their effect may be ranked as a sequence as follows: mole ratio of absolute alcohol to tetraethyl orthosilicate > solution pH value > mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate > ultrasonic wave power > mole ratio of deionized water to tetraethyl orthosilicate. The optimal processing parameters are as follows: solution pH value 2.68, ultrasonic wave power 113 W, mole ratio of deionized water to tetraethyl orthosilicate 9.03, mole ratio of absolute alcohol to tetraethyl orthosilicate 5.22, mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate 0.51.

Keywords
inorganic non-metallic materials, hexadecanol-palmitic acid-lauric acid, SiO2, humidity controlling performance, temperature controlling performance, optimized preparation

Introduction

Phase change energy storage materials can solve the contradiction between energy supply and demand in terms of time and space, improving energy utilization efficiency, and represent one of the hot topics in energy utilization and materials science research both domestically and internationally [1-4]. Organic phase change materials exhibit no supercooling or phase separation during phase transition and have stable chemical properties, thus finding wide application. However, there are very few organic phase change materials suitable for building applications with appropriate phase transition temperatures, and their cost is high. Recent research on organic phase change materials has focused on composite systems of binary phase change materials with inexpensive porous inorganic materials (SiO2) [5-8], while studies on ternary phase change systems combined with SiO2 are relatively scarce [9]. Meanwhile, research on SiO2 composite phase change materials has primarily focused on temperature control performance [10, 11], with little attention paid to the potential humidity control performance of SiO2 porous inorganic materials, such as the adsorption of water molecules by surface hydroxyl groups and nanoporous structures. This situation has resulted in SiO2-based composite phase change materials that can only improve indoor thermal comfort unilaterally, without improving indoor humidity comfort, greatly limiting their application in the building sector.

Based on the above analysis, this study prepared hexadecanol-palmitic acid-lauric acid/SiO2 composite phase change and humidity control materials using SiO2 as the carrier material and a ternary phase change system of hexadecanol-palmitic acid-lauric acid as the phase change material via the sol-gel method [12]. Additionally, based on uniform design and multivariate nonlinear regression equations, we investigated the effects of solution pH value, ultrasonic power, mole ratio of deionized water to tetraethyl orthosilicate, mole ratio of absolute

alcohol to tetraethyl orthosilicate, and mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate on the humidity control and temperature control performance of hexadecanol-palmitic acid-lauric acid/SiO2 composite materials, establishing an optimized preparation model and scheme.

1 Experimental Methods

1.1 Materials

The main raw materials included: tetraethyl orthosilicate (Si(OC2H5)4), analytical grade; absolute ethanol (CH3CH2OH), analytical grade; hexadecanol (C16H34O), analytical grade; palmitic acid (C16H32O2), analytical grade; lauric acid (C12H24O2), analytical grade; hydrochloric acid (HCl), analytical grade; and ammonia water (NH3·H2O), analytical grade. All experimental water used was deionized water.

1.2 Preparation Process

The preparation process was as follows: Hexadecanol, palmitic acid, and lauric acid were mixed at a mass fraction ratio of 30%:20%:50% in a beaker, then dissolved and stirred for 2 h at 60°C in a water bath to obtain a uniform dispersion, yielding the hexadecanol-palmitic acid-lauric acid mixture. A measured amount of tetraethyl orthosilicate was sequentially combined with specific quantities of absolute ethanol and deionized water in a beaker, then stirred for 10 min at medium speed using a constant-temperature magnetic stirrer in a 60°C water bath. The resulting mixture was dispersed in an ultrasonic cell disruptor for 15 min, after which the pH was adjusted to the target value using hydrochloric acid and ammonia water. After further ultrasonic dispersion for 15 min, the SiO2 sol was obtained. A predetermined amount of hexadecanol-palmitic acid-lauric acid was added to the SiO2 sol, then stirred at high speed for 15 min using a constant-temperature magnetic stirrer in a 60°C water bath, followed by ultrasonic dispersion for 45 min to uniformly distribute the hexadecanol-palmitic acid-lauric acid within the SiO2 carrier. The resulting hydrosol was aged for 2 h at 60°C in a constant-temperature water bath to form a gel, which was then dried in an oven at 80°C for 8 h to obtain the hexadecanol-palmitic acid-lauric acid/SiO2 composite phase change and humidity control material.

1.3 Performance Testing

Humidity control performance was tested using the isothermal moisture adsorption/desorption method [13-14]. The procedure involved: weighing 5 g of sample and drying it in an oven; when the mass difference between three consecutive weighings at 24 h intervals was less than 0.1%, the sample was considered completely dry. The dried sample was placed on a shelf above saturated salt solutions in a desiccator. When the mass difference between three consecutive weighings at 24 h intervals was less than 0.1% at a given relative humidity, the sample was considered to have reached moisture adsorption equilibrium. The

sample was then placed in another relative humidity environment. This process was repeated, periodically weighing the sample after it reached equilibrium in each humidity environment. Seven relative humidity environments were used in total (Table 1), ranging from 32.78% to 97.30%. The desorption test procedure was identical. The equilibrium moisture content (g/g) of the sample was calculated using the formula where m0 is the mass of the dry sample (g) and m is the mass after adsorption/desorption (g).

Temperature control performance was tested using the cooling curve method [15]. The procedure involved: weighing 2.5 g of sample into a test tube, immersing a thermocouple temperature probe into the sample (maintaining consistent probe immersion depth when testing multiple samples), placing the test tube in a 40°C water bath until the sample temperature reached 30°C, then transferring it to a 10°C water bath until the temperature dropped to 15°C. Temperature data points were recorded every 5 s during the cooling process from 35°C to 15°C, and a cooling curve was plotted. The time required for the cooling process from 35°C to 15°C was used to indicate the strength of the temperature control performance.

1.4 Sample Characterization

The structure of the hexadecanol-palmitic acid-lauric acid/SiO2 composite was analyzed using a BRUKER UECIOR 22 Fourier transform infrared spectrometer: the dried sample was mixed with potassium bromide and pressed into a pellet, then tested at room temperature (25°C) over the absorption range of 4000-500 cm-1. Morphology was observed using a JSM-6510LV scanning electron microscope: the sample was fixed on a stub and sputter-coated with gold before testing (operating voltage: 0-25 kV, resolution: 1 nm). Phase transition temperature and latent heat were measured using a TA2910 differential scanning calorimeter: the sample was placed in the sample pan and tested at a heating/cooling rate of 5°C/min under N2 atmosphere with a flow rate of 50 mL/min.

2 Results and Discussion

2.1 Uniform Design Experimental Results

This study investigated the effects of five factors on the humidity and temperature control performance of hexadecanol-palmitic acid-lauric acid/SiO2 composite materials: solution pH value (Factor A), ultrasonic power (Factor B), mole ratio of deionized water to tetraethyl orthosilicate (Factor C), mole ratio of absolute alcohol to tetraethyl orthosilicate (Factor D), and mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate (Factor E). Following a 5-factor, 5-level uniform design scheme (Table 2), the humidity control performance of the composite materials was tested using the isothermal adsorption/desorption method (Table 3), and temperature control performance was tested using the cooling curve method (Figure 1 [Figure 1: see original paper]).

As shown in Table 3, under the relative humidity condition of 97.30%, the equilibrium moisture content of the composite materials ranked as: 7# > 8# > 9# > 6# > 10# > 3# > 1# > 2# > 4# > 5#. The ranking of equilibrium moisture content under other relative humidity conditions was essentially the same, indicating that samples 7# and 9# exhibited better humidity control performance. Figure 1 shows that the time required for the cooling process of the composite materials ranked as: 2# > 1# > 6# > 4# > 3# > 5# > 10# > 8# > 7# > 9#, suggesting that samples 2# and 1# possessed stronger temperature control performance. A comprehensive analysis of Table 3 and Figure 1 reveals that the humidity control and temperature control performance of the composite materials exhibit a trade-off relationship.

2.2 Analysis of the Optimization Preparation Model

Based on the above analysis and according to Table 3 and Figure 1, a multivariate nonlinear regression equation was used to fit the relationship between factors and target values, establishing a model to optimize and evaluate the factor levels and their interactions. A quadratic regression equation [16, 17] was selected for this purpose. Considering the trade-off relationship between humidity control and temperature control performance, the target value Y was defined as Y = Y1 + Y2 (Table 4), where Y1 represents the normalized average of adsorption and desorption equilibrium moisture content at 97.30% relative humidity, and Y2 represents the normalized cooling time from 35°C to 15°C.

Table 5 presents the correlation coefficients for Y, where the regression coefficient Beta reflects the change in Y caused by each term, and the standardized coefficient Bt reflects the importance of each term' s influence on Y. The results show good agreement between the uniform design results and the quadratic regression model (R = 0.9982), indicating excellent regression performance for the quadratic model describing the humidity and temperature control performance of the composite materials. Table 5 also reveals that the importance ranking of factors affecting the target value Y is: Factor D (mole ratio of absolute alcohol to tetraethyl orthosilicate) > Factor A (solution pH value) > Factor E (mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate) > Factor B (ultrasonic power) > Factor C (mole ratio of deionized water to tetraethyl orthosilicate).

Based on the regression coefficients in Table 5, the quadratic regression equation for the target value Y, representing the combined humidity and temperature control performance, was established. The equation incorporates the main effects of all five factors with their respective coefficients as shown in Table 5.

2.3 Optimization Results

Using the Gauss-Newton algorithm [18-19] to solve the quadratic regression equation, the optimal preparation conditions were obtained: Factor A (solution pH value) = 2.68, Factor B (ultrasonic power) = 113 W, Factor C (mole ratio

of deionized water to tetraethyl orthosilicate) = 9.03, Factor D (mole ratio of absolute alcohol to tetraethyl orthosilicate) = 5.22, and Factor E (mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate) = 0.51. Under these conditions, the composite material exhibits the best humidity control and temperature control performance. The target value Y calculated from the quadratic regression equation is 1.5862.

Based on the experimental methods, performance testing, and characterization, the humidity control effects, temperature control effects (Figure 2 [Figure 2: see original paper] and Figure 3 [Figure 3: see original paper]), FT-IR results (Figure 4 [Figure 4: see original paper]), SEM results (Figure 5 [Figure 5: see original paper]), and DSC results (Figure 6 [Figure 6: see original paper]) of the optimally prepared composite material were obtained.

Figures 2 and 3 show that for the optimally prepared composite material at 97.30% relative humidity, the average of adsorption and desorption equilibrium moisture content is 0.1759 g/g, giving Y1 = 0.1759/0.2301 = 0.7645, indicating good humidity control performance. The cooling time from 35°C to 15°C is 1400 s, giving Y2 = 1400/1870 = 0.7487, indicating good temperature control performance. The target value Y for the optimized composite material is 1.5132, which is higher than the target values Y in Table 4, demonstrating excellent combined humidity and temperature control performance. Compared with the calculated target value Y of 1.5862 from the quadratic regression equation, the relative error is only -4.602%, confirming that the quadratic regression equation is valid for predicting the performance of the composite material.

The humidity control performance of the optimized composite material shows equilibrium moisture content of 0.0883-0.1045 g/g for adsorption and 0.0990-0.1153 g/g for desorption within the comfortable humidity range of 40%-65%. The phase transition temperature is between 24-28°C, close to human comfort temperature. These results demonstrate that the hexadecanol-palmitic acid-lauric acid/SiO2 composite phase change and humidity control material is suitable for building applications, maintaining stable indoor temperature and relative humidity through moisture and heat adsorption/desorption, thereby significantly improving indoor environmental comfort.

Figure 4 presents the FT-IR spectra of SiO2, hexadecanol-palmitic acid-lauric acid, and the composite material. In Figure 4a, characteristic SiO2 absorption peaks appear at 1056.47 cm-1 (asymmetric stretching vibration of cyclic Si-O-Si), 792.75 cm-1 (symmetric stretching vibration of Si-O-Si), and 933.75 cm-1 (bending vibration of Si-OH). In Figure 4b, peaks at 2917.05 cm-1 and 2849.35 cm-1 correspond to C-H stretching vibrations from CH3 and CH2 asymmetric and symmetric stretching, while peaks at 1464.88 cm-1 and 939.35 cm-1 arise from in-plane and out-of-plane bending vibrations of -OH groups, and the peak at 1706.44 cm-1 represents C=O stretching vibration, indicating that hexadecanol-palmitic acid-lauric acid exists mainly in the form of carboxylic acid dimers. Comparing Figure 4c with Figures 4a and 4b, all characteristic peaks of SiO2 and hexadecanol-palmitic acid-lauric acid appear in the compos-

ite material at 2917.34, 2849.75, 1710.27, 1466.16, 1057.93, 938.40, and 800.03 cm-1, with only slight shifts and intensity changes, indicating that no significant chemical reaction occurred between hexadecanol-palmitic acid-lauric acid and SiO2, but rather physical embedding.

Figure 5 shows the SEM images of SiO2 and the composite material. Figure 5a reveals that SiO2 exhibits a sponge-like structure with particles aggregated and connected by short necks to form a three-dimensional network structure, creating numerous pores with clear structure and small size. Figure 5b shows that the composite material appears as irregular particles, resembling multiple small spherical bodies connected in series with some agglomeration. These results demonstrate that hexadecanol-palmitic acid-lauric acid effectively intercalated into the SiO2 pores through the sol-gel process. This interpenetration and the encapsulation effect of SiO2 provide good form-stable properties. The smooth surface of the composite material with minimal phase change material deposition (Figure 5b) facilitates the adsorption of water molecules by SiO2 surface hydroxyl groups and nanoporous structures, thereby enhancing humidity control performance.

Figure 6 presents the DSC results for hexadecanol-palmitic acid-lauric acid and the composite material. Figure 6a shows that hexadecanol-palmitic acid-lauric acid has a phase transition temperature of 22.79-28.18°C and latent heat of 173.36-178.72 J/g. Figure 6b shows that the composite material has a phase transition temperature of 21.54-27.05°C and latent heat of 88.67-91.35 J/g. The phase transition temperature difference between the composite material and the pure phase change material is only 1.13-1.25°C, indicating that SiO2 as a carrier material has minimal effect on the phase transition temperature, which is primarily determined by the properties of hexadecanol-palmitic acid-lauric acid.

3 Conclusions

1. The three-dimensional network structure of SiO2 encapsulates hexadecanol-palmitic acid-lauric acid, utilizing its latent heat to provide temperature control performance, while the surface hydroxyl groups and nanoporous structure of SiO2 adsorb water molecules from air to provide humidity control performance.

2. Through uniform design combined with multivariate nonlinear regression analysis, the importance ranking of factors affecting the humidity and temperature control performance of hexadecanol-palmitic acid-lauric acid/SiO2 composite materials was determined as: mole ratio of absolute alcohol to tetraethyl orthosilicate > solution pH value > mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate > ultrasonic power > mole ratio of deionized water to tetraethyl orthosilicate.

3. The optimal preparation scheme for the composite material is: solution pH

value of 2.68, ultrasonic power of 113 W, mole ratio of deionized water to tetraethyl orthosilicate of 9.03, mole ratio of absolute alcohol to tetraethyl orthosilicate of 5.22, and mole ratio of hexadecanol-palmitic acid-lauric acid to tetraethyl orthosilicate of 0.51.

4. The composite material prepared according to the optimal scheme exhibits excellent humidity control and temperature control performance.

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