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Construction and performance test of high stability heat storage microcapsules based on physical regulation of nano-SiO₂

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ABSTRACT

To address the challenges of low strength, leakage risk, and toxic effluent pollution associated with paraffin phase change microcapsules used in deep mine thermal storage backfill, this study introduces nano-silica (nano-SiO₂) via in-situ polymerization for physical modification. High-performance paraffin/urea-formaldehyde resin phase change microcapsules (PUF-PCMs) were fabricated, and their structure, thermo-mechanical properties, and environmental benefits were systematically investigated. The results indicate that 2% is the optimal (nano-SiO₂) dosage. At this concentration, the microcapsules exhibit a regular spherical morphology with a dense and smooth surface, a melting temperature of 45.9°C, a latent heat of 141.8 J/g, and an encapsulation efficiency of 76.1%. Driven by the heterogeneous nucleation effect, the supercooling degree decreases from 9.1°C to 7.4°C. Macro-mechanical testing confirms that the compressive strength of the backfill containing PUF-PCMs is significantly superior to that of the group with direct paraffin addition, successfully maintaining the integrity of the backfill's mechanical skeleton. Furthermore, owing to the physical adsorption and hydrogen bonding of (nano-SiO₂), the removal rate of free formaldehyde in the effluent reaches 22.3%, offering distinct environmental benefits. This study validates a feasible approach for fabricating high-performance PUF-PCMs and managing thermal hazards in mines..

Keywords: Phase change materials; Urea-formaldehyde resin; Paraffin microcapsules; Nano-SiO₂; Thermal energy

storage properties

1. Introduction

With the progressive depletion of shallow-seated mineral resources and the continuous advancement of industrialization and urbanization, the imbalance between mineral supply and demand in China has become increasingly prominent. Consequently, deep-level mining has emerged as an inevitable strategic choice to address resource scarcity [1]. Deep mining operations face prominent geological characteristics known as the 'three highs', among which high geothermal temperature represents one of the most critical safety hazards in deep mines [2]. According to statistics, the temperature at some deep mine development faces has exceeded 40°C, which severely threatens the health of miners and production safety, while also restricting the improvement of mining efficiency [3]. Traditional backfill materials and technologies can no longer satisfy the requirements of deep mining for high efficiency, safety, and environmental protection. Consequently, there is an urgent need for novel backfilling materials with thermal regulation capabilities.

Phase change materials (PCM) represent a class of functional materials capable of absorbing or releasing substantial quantities of latent heat through phase transitions within a narrow temperature range. This characteristic enables high-density thermal energy storage and release under near-isothermal conditions, demonstrating vast application potential in fields such as building energy conservation [4,5], solar energy harvesting [6], thermal management of electronics [7], and thermal energy storage in mining engineering [8]. Integrating PCM into mining backfilling materials to construct thermal energy storage backfilling systems constitutes a pivotal technological pathway for alleviating thermal hazards in deep mines and achieving the synergistic exploitation of geothermal resources [9]. Among various organic PCM, paraffin is regarded as one of the most promising core materials for engineering applications, owing to its high latent heat (150-250 J/g), excellent chemical stability, non-corrosive nature, and cost-effectiveness [10,11]. Nevertheless, the practical deployment of paraffin is hindered by severe liquid-phase leakage during solid-liquid transitions and an intrinsically low thermal conductivity ($\sim 0.2 \text{ W/m}\cdot\text{K}$), which preclude its direct incorporation into backfilling matrices [12].

Microencapsulation technology, which involves fabricating a polymeric or inorganic shell around the paraffin core, not only effectively circumvents the leakage issue but also augments the contact area with heat transfer media. This approach significantly enhances thermal response, while simultaneously improving the chemical stability and cyclic durability of the materials [13,14].

Methodologies for the fabrication of paraffin microcapsules (MPCM) are broadly classified into three categories: chemical, physical, and physico-chemical techniques. Chemical methods encompass in-situ polymerization, interfacial polymerization, emulsion polymerization, and suspension polymerization [15]. Among these, in-situ polymerization is extensively favored owing to its technological maturity, superior encapsulation efficiency, and viability for large-scale production [16]. Regarding shell selection, commonly utilized polymeric shells include melamine-formaldehyde (MF) resin [17], urea-formaldehyde (UF) resin [18], polystyrene (PS) [19], and poly(methyl methacrylate) (PMMA) [20]. Inorganic shells, such as SiO_2 [21], TiO_2 [22], and CaCO_3 [23], have also been widely explored. Furthermore, organic–inorganic hybrid shells have garnered increasing attention due to their ability to synergistically integrate the merits of both constituents [24]. Urea-formaldehyde (UF) resin stands as one of the most prevalent industrial shell materials because of its abundant precursors, straightforward synthesis, cost-efficiency, and excellent interfacial compatibility with paraffin cores [25]. Nevertheless, pure UF resin shells are plagued by inherent limitations, such as insufficient mechanical strength, suboptimal thermal stability, and the emission of residual formaldehyde, which collectively constrain the broad engineering deployment of PUF-PCM [26].

In recent years, the modification of polymer composites using nanomaterials has emerged as a global research hotspot. Nano-silica (nano- SiO_2), characterized by its high specific surface area, exceptional thermal stability, and robust mechanical strength, has demonstrated unique reinforcement effects in the field of composites [27]. Notably, the abundance of surface silanol groups (Si-OH) facilitates multifaceted physicochemical interactions between nano- SiO_2 and polymer matrices. Research has indicated that the incorporation of nano- SiO_2 into UF resin systems can enhance

material compactness via the filling effect, thereby concurrently improving the mechanical integrity and thermal stability of the resulting shell [28].

In the field of microcapsule research, Ji et al. [29] incorporated nano-SiO₂ during the fabrication of microcapsules, yielding a minimum 1.4-fold enhancement in mechanical strength. The resulting microcapsules exhibited a nanohardness of 0.33 GPa and a Young's modulus of 2.63 GPa, while maintaining a high average core content of 85.39%. Notably, the addition of nano-SiO₂ bolstered the thermal stability by more than 2.9 times, with a negligible mass loss of only 0.95% at 182.73 °C. Furthermore, molecular dynamics (MD) simulations conducted by Zhang et al. [30] elucidated that the hydrogen bonding between the surface Si-OH groups of nano-SiO₂ and the amide groups in the urea-formaldehyde (UF) resin effectively immobilizes polymer chain segments. This interaction reduces the free volume of the system and significantly enhances the structural densification. In a related study, Weng et al. [31] introduced nano-SiO₂ into UF resin-modified fast-growing wood systems. Their findings demonstrated that nano-SiO₂ not only reinforces the mechanical properties of the UF resin but also substantially mitigates formaldehyde emission via physical adsorption, achieving a dual functionality of mechanical reinforcement and environmental friendliness. Additionally, Deng et al. [32] systematically investigated the mechanical performance and thermal stability of nanocellulose-reinforced UF resins, revealing that the integration of nanofillers facilitates the formation of an efficient heat conduction network, thereby elevating the overall performance of the material. Furthermore, Qian et al. [33] conducted an in-depth investigation into the crystallization behavior of C18 phase change materials (PCM) confined within mesoporous nano-SiO₂. This work highlighted the synergistic influence of the pore confinement effect and hydrogen bonding on phase change characteristics, providing critical insights into the interfacial interaction mechanisms between inorganic nanomaterials and PCM.

Regarding applications in mining engineering, cemented paste backfill (CPB) technology utilizes cement as the binder and industrial solid wastes—such as coal gangue and tailings—as aggregates. The mixture is prepared by stirring with water and subsequently pumped into underground goafs, where it undergoes solidification to form a stabilized

backfill body with significant load-bearing capacity [34]. Beyond its structural roles in supporting the surrounding rock mass and mitigating surface subsidence, the backfill body serves as a versatile functional carrier. When integrated with PCM, it facilitates the in-situ thermal regulation of deep mine environments [35]. However, the direct incorporation of paraffin into the backfill matrix typically leads to a deterioration in mechanical strength and persistent liquid-phase leakage. Microencapsulation technology addresses these limitations by effectively sequestering the paraffin within a protective shell, thereby providing a robust and viable pathway for the engineering-scale implementation of phase-change heat-storage backfill materials.

Introducing nano-SiO₂ into the PUF-PCM system can enhance the mechanical properties and thermal stability of the UF shell via the physical filling effect. Simultaneously, its high specific surface area and active surface functional groups can reduce the release of free formaldehyde in the toxic effluent, thereby achieving a synergy between enhanced thermal storage performance and engineering environmental friendliness. However, systematic studies regarding the influence of nano-SiO₂ dosage on the comprehensive performance of PUF-PCMs remain scarce, and the quantitative relationship between the optimal dosage and microcapsule performance has not yet been fully clarified.

In this study, a series of nano-SiO₂ modified paraffin/urea-formaldehyde resin phase change microcapsules were fabricated via in-situ polymerization. Under a fixed core-to-wall ratio, the effects of various nano-SiO₂ dosages (0%-4%) on the micromorphology, crystallization behavior, thermal storage characteristics, and environmental benefits of the microcapsules were systematically investigated. Concurrently, the modified microcapsules were incorporated into cemented backfill matrices for deep mines to explore their protective mechanisms on the macroscopic compressive strength of the backfill. This work aims to identify the optimal nano-SiO₂ modification dosage, thereby providing a critical material foundation and theoretical basis for the development and green engineering application of thermal storage backfill materials in deep, high-stress mines.

2 Experimental

2.1 Materials

The experimental materials and reagents used in this study are as follows: solid paraffin wax (melting point 45-48 °C, ΔHc = 186 J/g); formaldehyde solution (37 wt%, analytical reagent (AR) grade); urea (AR grade); Triton X-100 (chemical grade); and nano-SiO₂ (particle size 20 nm, purity > 99.8%). Other reagents, including citric acid, triethanolamine, and anhydrous ethanol (all AR grade).

The cementitious materials used in this study included cement, sourced from Shanshui Cement Group, and fly ash, provided by the Huangdao Power Plant in Qingdao. Coal gangue was obtained from the Daizhuang Coal Mine of Zikuang Group in Shandong Province, which was subsequently crushed and screened to achieve a particle size ≤ 25 mm. The particle size distribution of the coal gangue and the mix design of the filling materials were determined based on our previous research [36]. The mass ratio of cement, fly ash, and coal gangue was set at 1:4:6. The detailed methodologies for evaluating the mechanical properties are specified in Section 2.4.5.

2.2 Sample preparation

A single-variable control approach was employed in this study. The dosages of the core material paraffin (37.4 g), formaldehyde solution (18 mL), urea (30 g), and the emulsifier Triton X-100 were kept constant, while the nano-SiO₂ content was varied as the sole independent variable. Specifically, five dosage gradients (0%, 1%, 2%, 3%, and 4%) were established to systematically investigate their effects on the comprehensive performance of the PUF-PCM. The detailed experimental protocol is summarized in Table 1.

Table 1

Experimental design

Experimental	nano-SiO ₂	37%Formaldehyde/ml	Urea/g	Paraffin wax/g	Emulsifier/ml
A0	0%	18	30	37.4	1

A1	1%	18	30	37.4	1
A2	2%	18	30	37.4	1
A3	3%	18	30	37.4	1
A4	4%	18	30	37.4	1

2.3 Preparation of PUF-PCM

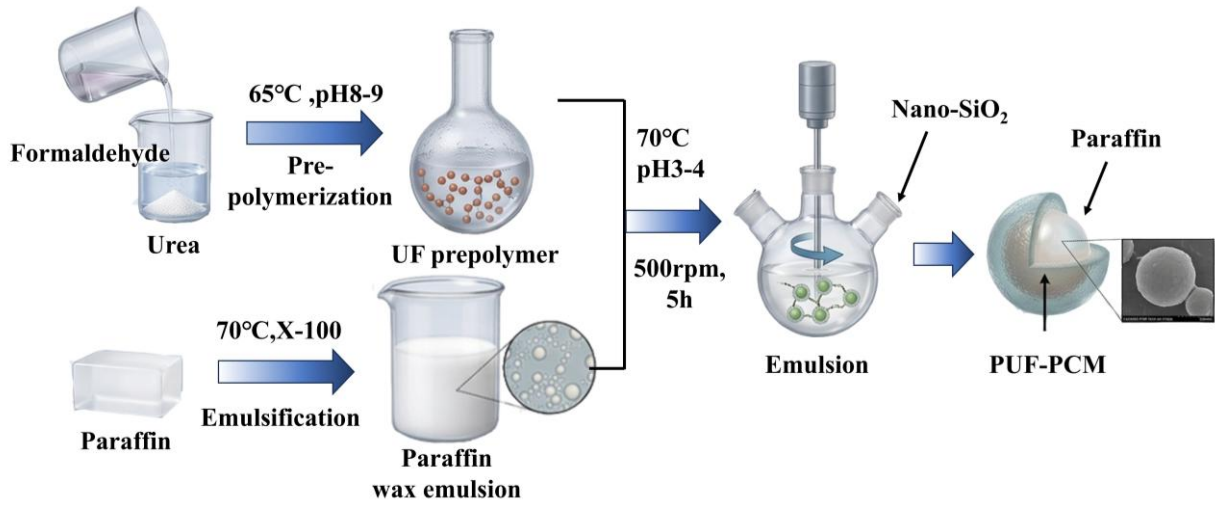
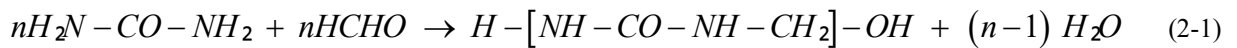


Fig. 1. Schematic of PUF-PCM preparation process

(1) Synthesis of the UF prepolymer: The formaldehyde solution (37 wt%) and urea were charged into a three-necked round-bottom flask at a molar ratio of 2:1. The pH of the system was adjusted to 8-9. The reaction mixture was stirred at 300 r/min and maintained at a constant temperature of 65°C using a thermostatic magnetic stirrer for 1 h to yield the UF prepolymer solution, which was stored for subsequent use. The reaction equation is expressed as follows (Eq. 2.1):



(2) Preparation of the paraffin emulsion: 1 mL of Triton X-100 was dissolved in 100 mL of ultrapure water and transferred into a three-necked flask. After raising the temperature to 70°C, the solid paraffin was added. The mixture was emulsified under constant stirring at 800 r/min for 30 min to form a paraffin oil-in-water (O/W) emulsion.

(3) Encapsulation and curing: The stirring speed was reduced to 600 r/min, and the UF prepolymer solution was

added dropwise, followed by stirring for 20 min. Subsequently, the pH of the system was adjusted to 3-4. The reaction was allowed to proceed continuously at a constant temperature of 70°C for 5 h to complete the encapsulation and curing of the shell layer.

(4) According to the dosages designed in Table 1 (0%-4%), the nano-SiO₂ dispersions, which had been pre-sonicated for 30 min, were added to the mixture. Stirring was continued at 70°C for another 2 h to ensure that the nano-SiO₂ particles were fully embedded into the shell layer.

(5) Post-treatment: The resulting product was isolated by centrifugation, washed, and dried to obtain a white microcapsule powder. The powder was then sealed and stored for subsequent use.

2.4 Fourier Transform Infrared Spectroscopy Analysis

The chemical structures of the samples were characterized using a Fourier transform infrared (FTIR) spectrometer (Bruker Tensor 27, Bruker, Germany). For sample preparation, the PUF-PCM powder was mixed with potassium bromide (KBr) at a mass ratio of 1:100 and finely ground until the particle size was less than 2 μm. The mixture was then pressed into pellets using the KBr pellet method. The infrared absorption spectra were recorded over a scanning range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ and an accumulation of 32 scans, using air as the background reference. For comparison, the FTIR spectra of pure paraffin and nano-SiO₂ were also measured under the same experimental conditions.

2.5. Scanning Electron Microscopy (SEM) Analysis

The surface morphology of the PUF-PCM microcapsules was characterized using a scanning electron microscope (SEM, Model Hitachi SU8010, Hitachi, Japan). For sample preparation, a small amount of PUF-PCM powder was dispersed in anhydrous ethanol and subjected to ultrasonication for 5-10 min. A few drops of the resulting suspension were cast onto a silicon wafer substrate and allowed to dry naturally at ambient temperature. To ensure electrical conductivity, the samples were subjected to gold sputter-coating under vacuum conditions and then affixed to the specimen stage using conductive adhesive tape. The SEM observations were conducted at an accelerating voltage of 5

kV and a working distance of 8 mm.

2.6 Differential Scanning Calorimetry (DSC) Analysis

The thermal properties of the PUF-PCM were characterized using a TA-Q200 differential scanning calorimeter (TA Instruments, USA). A sample mass of 6.0 ± 0.2 mg was weighed and sealed in an aluminum crucible, with an empty aluminum crucible serving as the reference. The measurements were conducted under a high-purity nitrogen atmosphere with a flow rate of 50 mL/min. Two heating-cooling cycles were performed within a temperature range of 15-75 °C at a constant heating and cooling rate of 10 °C/min. Data from the second cycle were recorded and analyzed to eliminate the influence of the thermal history of the material. The latent heat of phase change (ΔH) and the phase change temperature (T_m) were determined from the DSC curves. The latent heat of phase change is calculated according to Eq. (2-2) as follows:

$$\Delta H = A / m \quad (2-2)$$

where A represents the integrated area of the phase change peak on the DSC curve (J), and m is the mass of the sample (g).

The encapsulation efficiency (η) reflects the degree of retention of the latent heat of phase change of the paraffin wax after the microencapsulation process, The calculation is performed according to Eq. (2-3) as follows:

$$\eta = \Delta H_{m, capsule} / \Delta H_{m, paraffin} \times 100\% \quad (2-3)$$

where $\Delta H_{m, capsule}$ represents the melting latent heat of the microcapsules (J/g), and $\Delta H_{m, paraffin}$ denotes the melting latent heat of the pure paraffin (J/g). In this study, $\Delta H_{m, paraffin}$ is 186 J/g.

The degree of supercooling (ΔT) is employed to quantify the thermodynamic driving force during the crystallization process of phase change materials, The calculation is performed according to Eq. (2-4) as follows:

$$\Delta T = T_{pm} - T_{pc} \quad (2-4)$$

In this expression, T_{pm} and T_{pc} denote the peak melting temperature and peak crystallization temperature,

respectively (units in degrees Celsius).

2.7 High-performance liquid chromatography (HPLC)

The filtered effluent remaining after the fabrication of each PUF-PCM group was collected. Quantitative analysis of the residual formaldehyde in the effluent was performed via the 2,4-dinitrophenylhydrazine (DNPH) derivatization method using a high-performance liquid chromatography system (HPLC, Agilent 1260). The formaldehyde concentration in each effluent group and the adsorption removal efficiency of formaldehyde by nano-SiO₂ were calculated using the standard curve method.

2.8 Comparative study of macroscopic compressive strength

The raw materials were proportioned according to a predetermined mass ratio of cement, fly ash, and coal gangue (1:4:6), with the incorporation of PUF-PCM at specific dosages. The components were then thoroughly homogenized through mechanical stirring. Subsequently, a backfill slurry with a solid concentration of 68% was prepared by mixing the dry components with water. The resulting mixture was cast into standard cubic molds with dimensions of 70.7 mm x 70.7 mm x 70.7 mm. The specimens were then subjected to standard curing for 28 days at a temperature of 20±2 degrees Celsius and a relative humidity exceeding 95%. Following the curing period, the uniaxial compressive strength (UCS) was measured using an electronic universal testing machine at a constant loading rate of 0.5 mm/min. For each experimental group, three replicate specimens were tested, and the average value was recorded as the final result.

3 Results and Discussion

3.1 FTIR Characterization

The infrared absorption spectra of the PUF-PCMs were recorded using a Fourier transform infrared spectrometer, and the results are illustrated in the figure below. Analysis of Fig. 2 reveals that pure paraffin exhibits strong and sharp absorption peaks at 2920 cm⁻¹ and 2850 cm⁻¹, which correspond to the asymmetric stretching and symmetric C-H stretching vibrations of -CH₂ and -CH₃ groups, respectively. The peak at 1473 cm⁻¹ is attributed to the scissoring vibration

of CH_2 , while the peak at 719 cm^{-1} represents the in-plane rocking vibration of long-chain methylene groups. These characteristic peaks are in excellent agreement with the standard spectra of n-alkanes. For nano- SiO_2 , a broad and intense absorption peak appears near 1104 cm^{-1} , which is assigned to the asymmetric stretching vibration of Si-O-Si. The peaks at 803 cm^{-1} and 470 cm^{-1} correspond to the symmetric stretching and bending vibrations of Si-O-Si, respectively. Furthermore, the broad peak at 3450 cm^{-1} is associated with the O-H stretching vibration of surface silanol (Si-OH) groups.

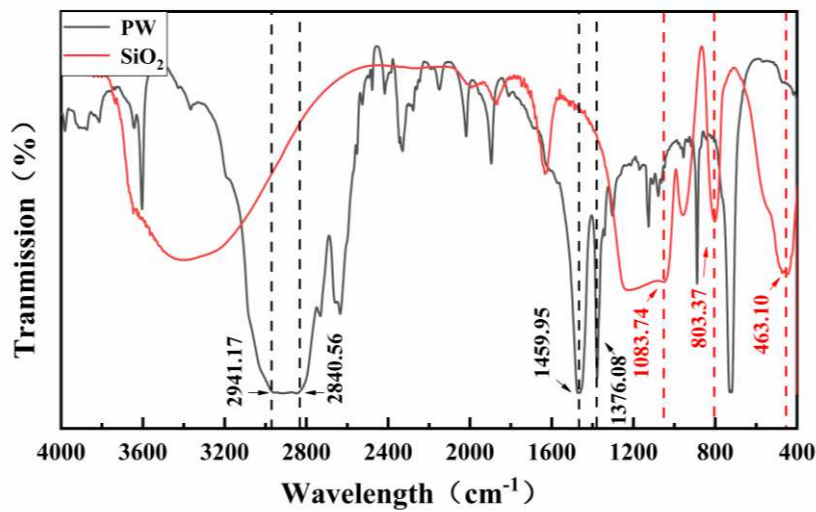


Fig. 2. FTIR spectra of paraffin and nano- SiO_2

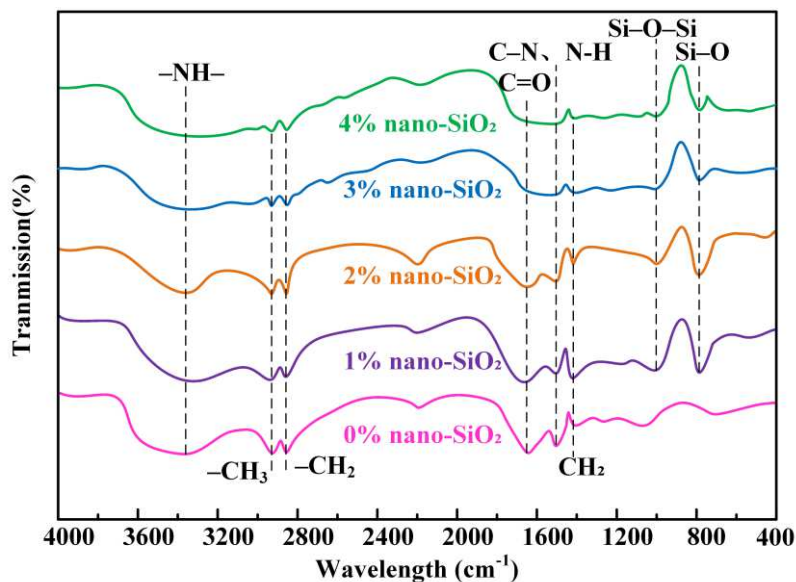


Fig. 3. FTIR spectra of PUF-PCM with different nano- SiO_2

As illustrated in Fig 3, all PUF-PCM samples exhibit a broad absorption band near 3335 cm^{-1} , which is attributed to

the N-H stretching vibration of the amide II band within the urea-formaldehyde (UF) resin. The absorption peak at 1640 cm^{-1} is assigned to the C=O stretching vibration, while the signal at 1545 cm^{-1} corresponds to the coupling of C-N stretching and N-H bending vibrations. Notably, the characteristic -CH₂- stretching vibration peaks of the paraffin core are preserved at 2920 cm^{-1} and 2850 cm^{-1} , confirming that the paraffin has been successfully encapsulated within the UF shell layer. As the nano-SiO₂ dosage increases from 0% to 4%, the intensity of the Si-O-Si asymmetric stretching vibration peak near 1100 cm^{-1} gradually intensifies, accompanied by the enhancement of the Si-O bending vibration peak at 800 cm^{-1} . This trend indicates the successful incorporation of nano-SiO₂ into the microcapsule system, with the actual loading showing a positive correlation with the designed addition amounts, thereby verifying the effective loading of nano-SiO₂.

In all PUF-PCM sample groups, no significant shifts or emergence of new peaks were observed for the Si-O-Si characteristic features. Furthermore, no new broad hydrogen-bonding peaks were detected within the 3200-3600 cm^{-1} range, and the positions of the C=O and N-H characteristic peaks of the UF resin remained highly consistent across all groups. These results indicate that no chemical bonding or significant specific hydrogen-bonding interactions occurred between the nano-SiO₂ and the UF resin matrix. Instead, nano-SiO₂ exists within the microcapsule shell through physical filling without altering the chemical structure of the UF resin. Consequently, the improvement of UF resin properties by nano-SiO₂ primarily stems from its filling effect on the free volume of polymer segments and the physical confinement at the interface, rather than from chemical reactions [37]. This physical embedding mode ensures that the chemical structure and intrinsic phase-change thermal properties of the paraffin core remain unaffected, providing a solid structural foundation for maintaining high latent heat.

3.2 Morphological analysis of paraffin microcapsules via SEM

The SEM images of the PUF-PCMs are shown in Fig. 4, systematically illustrating the influence of the nano-SiO₂ dosage on the microcapsule morphology. Analysis of Fig. 4 reveals that the microcapsules in all groups exhibit an overall spherical or quasi-spherical morphology, demonstrating that the in situ polymerization process achieved effective shell

encapsulation at the oil-water interface. In the control group A0 without nano-SiO₂ addition, several tiny pores and localized indentations are observed on the microcapsule surfaces, indicating a relatively loose shell structure. This phenomenon is attributed to the insufficient cross-linking density of the pure UF resin and the localized stress concentration induced by shrinkage during the polycondensation process. Such structural imperfections may serve as potential pathways for the leakage of the paraffin core material during thermal cycling.

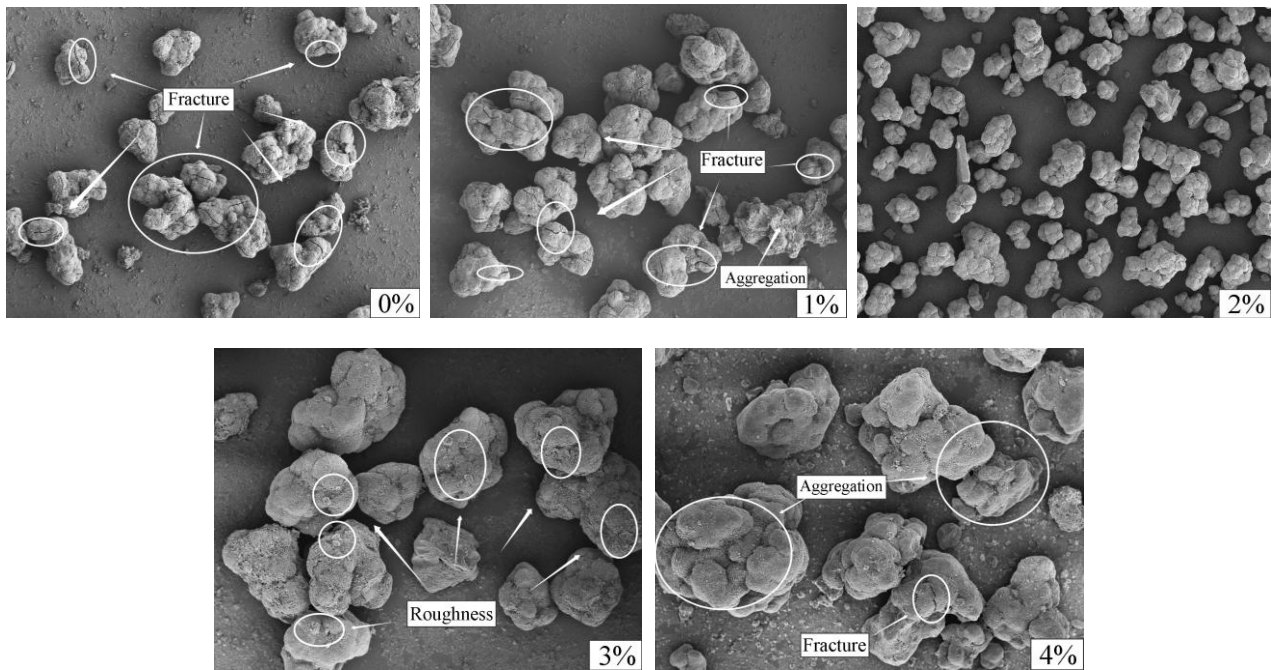


Fig. 4. SEM images of PUF-PCM with different nano-SiO₂ (x200)

When the nano-SiO₂ loading increases to 1%, the number of protuberant particles on the capsule surface increases, leading to a marked elevation in surface roughness. The embedding of primary nano-SiO₂ particles is observable in localized regions, accompanied by a reduction in pre-existing micropores. This indicates that nano-SiO₂ begins to fill the micro-defects of the shell, although the particle distribution remains non-uniform at this stage. As the loading further increases to 2%, the density of surface protrusions increases and the particle distribution becomes more homogeneous. The overall surface appears denser and smoother, with a significant decrease in crevices and voids, achieving optimal shell continuity. Meanwhile, the particle size of the microcapsules increases relative to groups A0 and A1, suggesting that the filling effect of nano-SiO₂ reaches an optimal equilibrium at this dosage—effectively repairing shell defects without

inducing significant particle aggregation. This observation is mutually corroborated by the moderate enhancement of the Si-O-Si peak intensity in the FTIR spectra.

With the nano-SiO₂ loading further increasing to 3% and 4%, prominent indentations, ruptures, and roughened regions emerge on the microcapsule surfaces. Hard agglomeration occurs among a portion of the particles, resulting in large-scale aggregates that detrimentally impact the structural integrity of the shell. This phenomenon is attributed to the diminished dispersibility of excessive nano-SiO₂ in the aqueous phase. The resulting agglomerates deposit onto the surface of the developing UF shell, hindering the uniform cross-linking of polymer segments. This introduces stress concentration sites within the shell architecture, thereby compromising the overall structural integrity and elevating the risk of core material leakage [38].

It can be concluded that at nano-SiO₂ loadings of 2% or less, the particles are predominantly embedded in the shell in a primary dispersed state, effectively filling micro-defects and maintaining shell integrity. In contrast, at loadings of 3% or higher, the hard agglomeration effect becomes dominant, leading to an increase in shell surface defects and a significantly higher risk of core material leakage. Consequently, 2% is identified as the optimal nano-SiO₂ dosage, enabling a comprehensive enhancement of performance while preserving the structural integrity of the shell.

3.3 Analysis of DSC Results

The DSC curves of the PUF-PCMs, measured within a temperature range of 15-75°C at a heating/cooling rate of 10°C/min under a N₂ atmosphere with a flow rate of 50 mL/min, are shown in Fig. 5; the data were extracted from the second cycle. As shown in Fig. 5, all samples exhibit a single symmetric endothermic peak during the heating process, corresponding to the solid-liquid melting phase transition of the paraffin core. During the cooling process, an exothermic peak is observed, representing the liquid-solid crystallization transition. The presence of a single phase-transition peak demonstrates that only a single paraffin component was encapsulated within the microcapsules, indicating that the encapsulation process is stable and controllable. Furthermore, the intrinsic chemical properties of the paraffin core

remained unaffected by the shell material, which is in good agreement with the conclusions drawn from the FTIR analysis.

Based on the integration analysis of the DSC curves, the thermal performance parameters of various PUF-PCM groups are summarized in Table. 2.

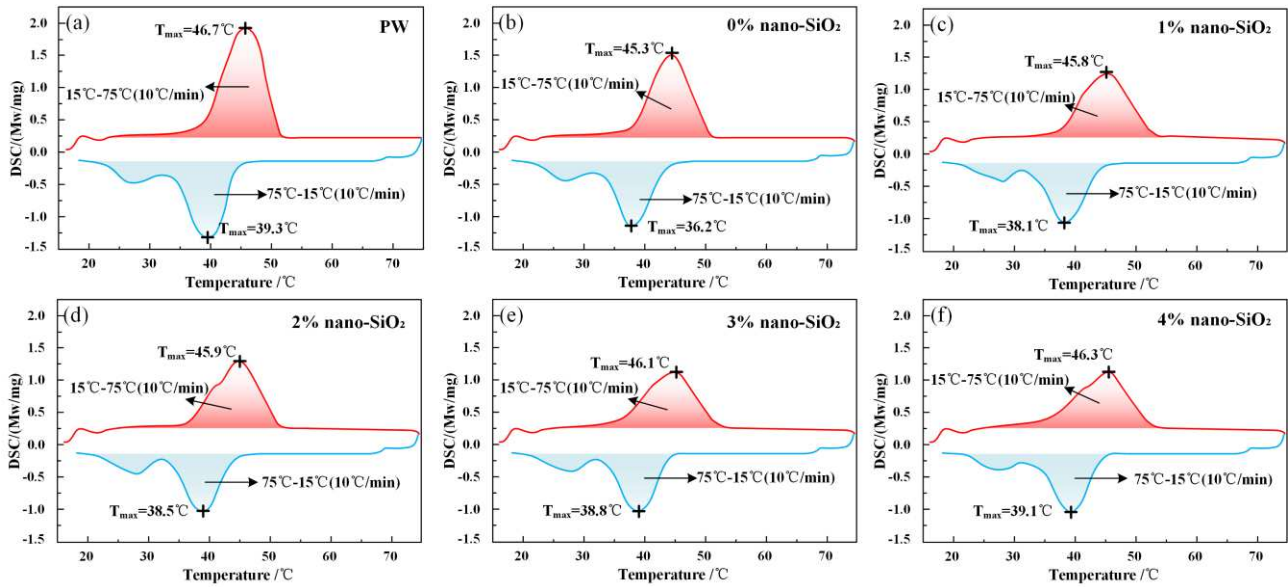


Fig. 5. DSC curves of PUF-PCM with different nano-SiO₂

As indicated in Table. 2, the control group A0 presents a peak melting temperature T_{pm} of 45.3 degrees Celsius, a melting enthalpy ΔH_m of 142.3 J/g, and an encapsulation efficiency η of 76.5%. Compared with pure paraffin ($\Delta H_m = 186$ J/g), the reduction in latent heat is primarily attributed to the presence of the UF shell, which constitutes approximately 23.5% of the total microcapsule mass. Since the shell does not contribute to the phase-change properties, this reduction is consistent with the expectations of the rule of mixtures for composite materials.

Table 2

Summary of DSC thermal performance parameters for PUF-PCM with varying nano-SiO₂ loadings.

Sample	T_{pm} (°C)	ΔH_m (J/g)	T_{pc} (°C)	$\Delta T = T_{pm} - T_{pc}$ (°C)	η (%)
PCM	46.7	186.0	39.3	7.4	-

A0 (0%)	45.3	142.3	36.2	9.1	76.5
A1 (1%)	45.8	141.5	38.1	7.7	76.1
A2 (2%)	45.9	141.8	38.5	7.4	76.2
A3 (3%)	46.1	139.5	38.8	7.3	75.0
A4 (4%)	46.3	137.2	39.1	7.2	73.8

Upon increasing the nano-SiO₂ loading to 1%, T_{pm} slightly increases to 45.8 degrees Celsius, while delta H_m remains essentially stable at 141.5 J/g. Notably, the peak crystallization temperature T_{pc} rises from 36.2 degrees Celsius to 38.1 degrees Celsius, resulting in a decrease in the supercooling degree delta T from 9.1 degrees Celsius to 7.7 degrees Celsius. This reduction in supercooling demonstrates that nano-SiO₂ particles function as heterogeneous nucleating agents during the crystallization of paraffin. These particles provide energetically favorable interfaces for the formation of paraffin nuclei, effectively lowering the nucleation barrier and facilitating crystallization at higher temperatures [39].

Further increasing the loading to 2% resulted in a T_{pm} of 45.9 degrees Celsius and a delta H_m of 141.8 J/g, which remained nearly invariant compared with group A1. T_{pc} rose to approximately 38.5 degrees Celsius, with a delta T of 7.4 degrees Celsius. This indicates that within the loading range of 1-2%, the number of heterogeneous nucleation sites provided by nano-SiO₂ tends toward saturation, and the supercooling degree no longer decreases significantly with further increases in content. Combined with SEM analysis, nano-SiO₂ is uniformly dispersed in this concentration range, ensuring sufficient interfacial contact with the paraffin and maximizing the nucleation effect. Simultaneously, nano-SiO₂ constructs more continuous thermal conduction pathways by filling shell micro-defects, which facilitates heat exchange between the interior and exterior of the microcapsules. This result is mutually corroborated by the optimal SEM morphology of group A2.

As the loading increased to 3%, T_{pm} rose slightly to 46.1 degrees Celsius, while ΔH_m decreased to 139.5 J/g with an η of 75.0%. For group A4, although T_{pc} reached 39.1 degrees Celsius and the supercooling degree ΔT was compressed to 7.2 degrees Celsius—representing the most significant numerical effect of heterogeneous nucleation—the DSC peaks exhibited marked broadening. This suggests that the hard agglomerates formed by excessive nano-SiO₂ introduced non-uniform thermal conduction pathways and phase-change inhibition effects within the shell, leading to a decline in the crystallization uniformity of the paraffin [40]. Furthermore, the evident decrease in ΔH_m for groups A3 and A4 is closely correlated with the increased shell rupture and surface defects observed in SEM. It is hypothesized that a portion of the paraffin leaked during the preparation and washing processes, resulting in a reduction in the actual mass of encapsulated paraffin.

By synthesizing the DSC thermal performance parameters and SEM morphological characterizations, it is concluded that the 2% nano-SiO₂ loading achieves the optimal balance of properties. With an encapsulation efficiency (η) of 76.1%, this dosage successfully reduces the supercooling degree from 9.1 degrees Celsius to 7.4 degrees Celsius without significantly compromising the thermal energy storage capacity. This enhancement effectively improves the thermal response rate of the microcapsules while maintaining superior shell morphological integrity, ultimately resulting in the best overall thermal performance.

3.4 High-performance liquid chromatography (HPLC)

The HPLC chromatograms of the formaldehyde-DNPH derivatives in the PUF-PCM effluents with different nano-SiO₂ dosages, along with the variations in formaldehyde removal efficiency and adsorption capacity per unit mass of nano-SiO₂ as a function of the dosage, are presented in Figures 6 and 7; the quantitative results are summarized in Table 3. As shown in this, the formaldehyde concentration in the effluent of the control group without nano-SiO₂ addition was 0.394 g/L. This residual formaldehyde primarily originates from the incomplete conversion of the polycondensation reaction of the UF resin and the partial hydrolytic release of formaldehyde-urea adducts during the acid-curing process.

With the increasing nano-SiO₂ loading, the formaldehyde concentration in the effluent exhibited a monotonic decreasing trend. In group A4, the formaldehyde concentration was reduced to 0.243 g/L, achieving a formaldehyde removal efficiency of 38.3%. This indicates that nano-SiO₂ exerts a significant physical adsorption effect on the free formaldehyde within the effluent.

Table 3

Quantitative analysis results of formaldehyde in the effluent at varying nano-SiO₂ loadings.

nano-SiO ₂ /wt%	formaldehyde / g/L	RSD/%	removal rate /%	adsorption rate / mg/g
0% (A0)	0.394	2.08	0	—
1% (A1)	0.332	0.60	15.7	53.3
2% (A2)	0.306	0.71	22.3	39.6
3% (A3)	0.275	2.33	30.2	36.7
4% (A4)	0.243	1.47	38.3	35.5

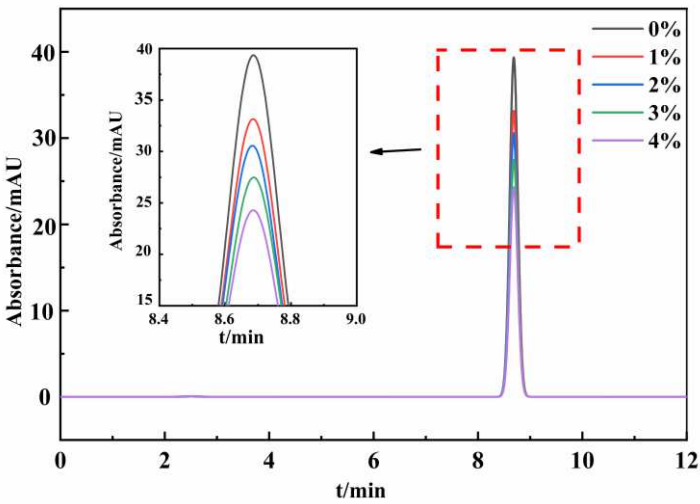


Fig. 6. HPLC chromatograms of formaldehyde-DNPH derivatives in wastewater

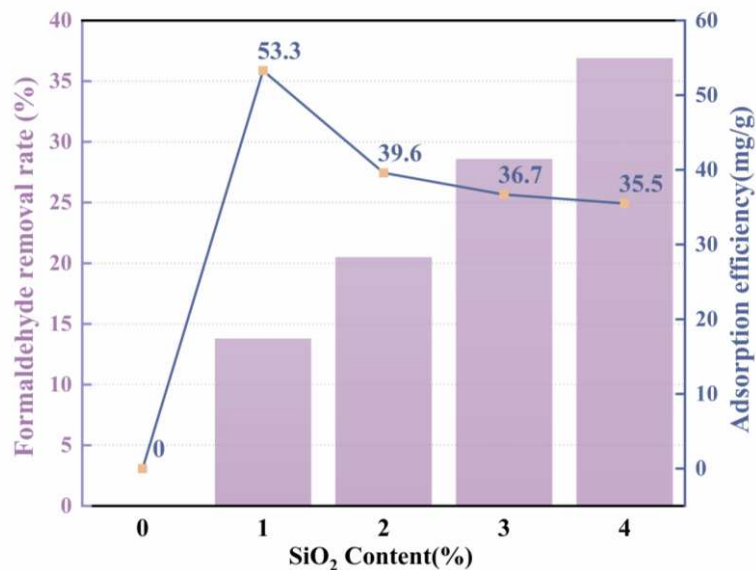


Fig.7. formaldehyde removal rate and adsorption efficiency

Based on the analysis of adsorption mechanisms, the sequestration of formaldehyde by nano-SiO₂ is primarily realized through the following pathways: The vast specific surface area of nano-SiO₂ (>200 m²/g) provides a multitude of physical adsorption sites. Furthermore, the abundant Si-OH (silanol) groups on the nano-SiO₂ surface can interact with the C=O groups of formaldehyde molecules via hydrogen bonding, forming a stable surface adsorbed state. This interaction effectively immobilizes formaldehyde on the nano-SiO₂ surface and minimizes its release into the liquid phase [41]. However, regarding the formaldehyde adsorption efficiency per unit mass of SiO₂ presented in Table 3, a progressive decline from 53.3 mg/g to 35.5 mg/g is observed as the loading increases from 1% to 4%. This trend reflects a gradual saturation effect of the adsorption sites. In the low-loading stage, the nano-SiO₂ particles are uniformly dispersed, allowing the surface active sites to be fully exposed, which results in the highest adsorption efficiency per unit mass. As the dosage increases, the degree of inter-particle agglomeration intensifies, leading to a relative reduction in the effective specific surface area available for adsorption. Consequently, the unit adsorption efficiency decreases accordingly. .

Synthesizing the indices of both removal and adsorption efficiency, the 4% nano-SiO₂ loading achieves the highest formaldehyde removal efficiency at approximately 38.3%. However, a systematic trade-off is necessitated when considering the detrimental impacts of excessive loading on the SEM micro-morphology and DSC thermal properties, as

well as the significant decline in unit adsorption efficiency. If the overall performance of the microcapsules is prioritized, the 2% nano-SiO₂ dosage exhibits superior comprehensive application value; it maintains a 22.3% formaldehyde removal efficiency while preserving the optimal morphological integrity and thermal characteristics of the microcapsules. These results demonstrate that the incorporation of nano-SiO₂ not only optimizes the functional properties of the microcapsules but also mitigates formaldehyde emissions during the fabrication process, thereby yielding significant environmental benefits.

3.5 Comparative Study of Macroscopic Compressive Strength

A comparison of the uniaxial compressive strength (UCS) among the blank backfill without PCMs, the backfill containing pure paraffin, and the backfill containing PUF-PCMs (with the optimal 2% nano-SiO₂ dosage selected based on the aforementioned study) after 28 days of standard curing is presented in Fig. 8. As clearly observed in Fig. 8, the compressive strengths of the three backfill groups exhibit pronounced disparities. The incorporation of pure paraffin results in a significant reduction in compressive strength compared to the blank control group. This degradation is attributed to the semi-solid state of paraffin at the curing temperature, which tends to form weak interfaces within the backfill, thereby disrupting the continuity of the cement-aggregate system. Furthermore, the migration of liquid paraffin induces the formation of macroscopic voids within the backfill, severely compromising its structural mechanical framework.

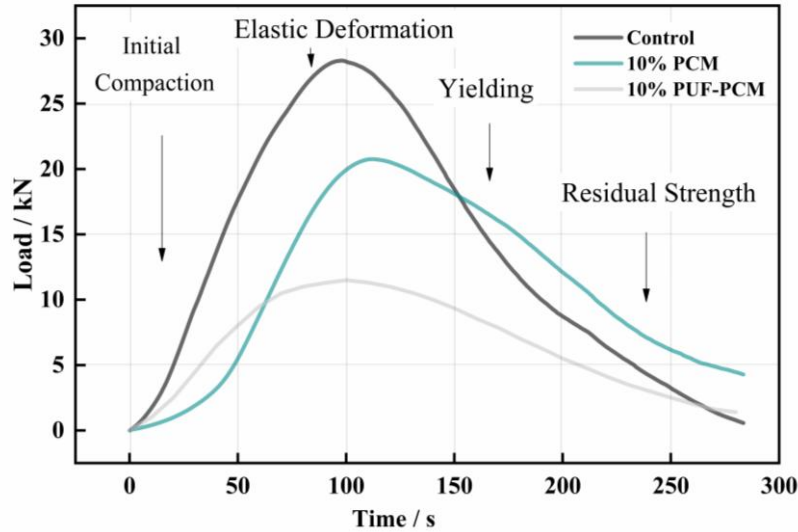


Fig. 8. Comparison of unconfined compressive strength of backfill specimens

In contrast, the backfill specimens containing PUF-PCM show significantly superior compressive strength compared to those with an equivalent mass of pure paraffin. This enhancement indicates that the microencapsulation process, facilitated by the UF polymer shell, effectively segregates the paraffin from the backfill matrix. This isolation prevents liquid paraffin from eroding the cement hydration products and weakening the aggregate interfaces. As rigid spherical particles, the microcapsules establish better interfacial contact with the hydration products, resulting in a relatively minimal impact on the mechanical properties. This further validates microencapsulation as an effective strategy for incorporating PCM into backfill materials. The intact shell not only resists external pressure to maintain the spherical morphology during curing and early loading but also effectively prevents paraffin leakage, ensuring the structural integrity of the backfill matrix.

The aforementioned macro-mechanical testing results validate the microscopic and thermal conclusions derived from the SEM and DSC analyses at an engineering application scale. The addition of PUF-PCMs provides the most significant protective effect on the compressive strength of the backfill, effectively maintaining its mechanical performance and presenting a feasible solution for the practical application of thermal storage backfill in deep mines.

4 Conclusions

In this study, a series of nano-SiO₂ modified paraffin/urea-formaldehyde resin phase-change microcapsules (PUF-PCM) were successfully synthesized via in situ polymerization. The influence of nano-SiO₂ dosage on the comprehensive performance of the microcapsules was systematically investigated through FTIR, SEM, DSC, UCS, and HPLC. The primary conclusions are as follows:

(1) Nano-SiO₂ is incorporated into the UF shell through a physical embedding mode, which preserves the chemical structures of both the urea-formaldehyde resin and the paraffin, thereby maintaining the intrinsic thermal properties of the phase-change material (PCM). At an optimal dosage of 2%, the microcapsules exhibit superior morphology, characterized by regular spherical shapes, dense and smooth surfaces, and high shell integrity. The thermal parameters include a peak melting temperature T_{pm} of 45.9 degrees Celsius, a latent heat of fusion ΔH_m of 141.8 J/g, and an encapsulation efficiency η of 76.1%. The supercooling degree ΔT was reduced from 9.1 degrees Celsius to 7.4 degrees Celsius, indicating that the heterogeneous nucleation effect significantly improved the crystallization kinetics of the paraffin. Conversely, at dosages of 3% or higher, hard agglomeration of particles leads to increased shell defects, resulting in a decline in both thermal performance and morphological quality.

(2) The microencapsulation process effectively encapsulates the paraffin within the UF shell to prevent leakage. The backfill containing PUF-PCMs exhibits the highest compressive strength, which is significantly superior to that of the backfill with direct paraffin addition. Furthermore, nano-SiO₂ exerts a physical adsorption and removal effect on the free formaldehyde in the toxic effluent, achieving a removal rate of 22.3% at a 2% dosage, thereby balancing both performance enhancement and environmental friendliness.

In summary, a 2% nano-SiO₂ loading is identified as the optimal dosage for fabricating high-performance PUF-PCM. The resulting microcapsules demonstrate exceptional performance in thermal energy storage efficiency, mechanical stability, and green synthesis, showing broad application prospects in the fields of thermal storage backfilling for deep mines and industrial thermal management.

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