Article

Silica-Based Core-Shell Nanocapsules: A Facile Route to Functional Textile

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Abstract: In this work, we present a surfactant-free miniemulsion approach to obtain silica-based core-shell nanocapsules with a phase change material (PCM) core via in-situ hydrolytic polycondensation of precursor hyperbranched polyethoxysiloxanes (PEOS) as silica shells. The obtained silica-based core-shell nanocapsules (PCM@SiO₂), with diameters of ~400 nm and silica shells of ~14 nm, reached the maximum core content of 65%. The silica shell had basically no significant influence on the phase change behavior of PCM, and the PCM@SiO₂ exhibited a high enthalpy of melt and crystallization of 123–126 J/g. The functional textile with PCM@SiO₂ has been proposed with thermoregulation and acclimatization, ultraviolet (UV) resistance and improved mechanical properties. The thermal property tests have shown that the functional textile had good thermal stability. The functional textile, with a PCM@SiO₂ concentration of 30%, was promising, with enthalpies of melting and crystallization of 27.7 J/g and 27.8 J/g, and UV resistance of 77.85. The thermoregulation and ultraviolet protection factor (UPF) value could be maintained after washing 10 times, which demonstrated that the functional textile had durability. With good thermoregulation and UV resistance, the multi-functional textile shows good prospects for applications in thermal comfort and as protective and energy-saving textile.

Keywords: functional textile; silica-based core-shell nanocapsules; phase change material; thermal regulation; thermal energy storage; anti-ultraviolet

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1. Introduction

Thermal regulation and acclimatization properties of textiles are important factors for comfort. The latent heat-storage material, phase change material (PCM), has become the most efficient and cost-effective for a variety of thermal energy storage and thermal regulation applications, due to the ability to store heat and consume at a later time [1–4]. PCM can absorb, store or release a large amount of energy in the form of latent heat within a narrow temperature range during its phase transition, which attracted interest for astronauts' space suits during the early 1980s [5,6] for withstanding the temperature fluctuations in outer space. According to their initial and final phase, PCM could be solid-solid, solid-liquid, solid-gas, liquid-gas or vice versa [7]. Actually, PCM with solid-liquid phase transition is the most widely used variety due to its high heat-storage capacity. They have been widely employed in solar energy storage [8], building applications [9], the food industry [10] and pharmaceutical applications [11]. PCM has also been incorporated into wearables such as gloves, shoes, coats, and sleep bags as a smart textile [12]. Paraffin was found to be one of the most promising PCMs for textiles. Embedding PCM inside fabrics for apparel and decoration textiles can improve human comfort and reduce indoor energy

use [13,14]. However, the transition from solid to liquid phase leads to severe issues such as outflow of paraffin, instigating physical distortion.

PCM encapsulation is requisite and vital for preventing phase separation, preserving optimal utilization. The encapsulated PCM can be directly applied to textile materials (fibers, fabrics) such as yarns, clothes, curtains and wall decoration fabrics. Therefore, stable chemical properties, lack of toxicity and comfort are required of encapsulated PCMs. Recently, most paraffin used in cores has been encapsulated in organic shells, such as melamine-formaldehyde resin [15], polystyrene [16], polymethylmethacrylate [17] and cellulose [18]. However, the disadvantages of polymeric shells, such as poor stability, biological safety and flammability limited applications [19]. Therefore, inorganic shell materials, such as CaCO_3 [20], TiO_2 [21], Al_2O_3 [22] and SiO_2 [23], have attracted attention because of a number of useful features. Especially, silica materials are particularly noteworthy due to their availability, low cost, good thermal conductivity, chemical inertness, excellent stability and mechanical strength, and biocompatibility [24]. Silica nanoparticles also have a strong ability to reflect ultraviolet light. For silica encapsulating of PCMs, spray drying [25], sol-gel [26] and interfacial polymerization [27] have been explored. The most commonly synthesized silica nanocapsules were fabricated from emulsion with tetraethoxysilane (TEOS) as the silica precursor by adding surfactants to increase emulsion stability [28,29]. As we know, lots of surfactants were available for this use in various industries, but they were unable to achieve the requirements for non-toxicity, environmental protection and sustainable development [30]. In recent years, we have synthesized the amphiphilic silica precursor, poly(ethylene glycol) substituted hyperbranched polyethoxysiloxane (PEG-PEOS), and constructed silica nanocapsules loading enzymes by self-assembly of the amphiphilic silica precursor, surfactants-free due to its high solubility and rapid reaction in the water [31,32]. With the development of this research, we found that the hyperbranched poly-ethoxysiloxane (PEOS) molecules were insoluble in water, but could simultaneously show pronounced amphiphilicity induced by hydrolysis at the *oil/water* interfaces.

In this work, we have presented a surfactant-free miniemulsion approach to obtain silica-based core-shell nanocapsules with PCM cores via in-situ hydrolytic polycondensation of precursor hyperbranched polyethoxysiloxanes (PEOS) as well as emulsion stabilizers. The evaluation of the morphology, encapsulated ratio, thermal properties, mechanical properties and leakage prevention of silica-based nanocapsules give them a potential use as novel energy-storage materials for thermal regulation and ultraviolet blocking in multi-functional textiles.

2. Materials and Methods

2.1. Materials

Silica precursor hyperbranched polyethoxysiloxanes (PEOS) were synthesized in a lab according to the guidelines in the literature [33]. Tetraethoxysilane (2.0 mol) was mixed with acetic anhydride (2.1 mol) and titanium trimethylsiloxide (6.0 mmol) under a nitrogen atmosphere in a three-neck round-bottomed flask equipped with a stirrer at 300 rpm, connected with a distillation bridge. The mixture was heated to 135 °C in a silicon oil bath under intensive stirring. The resulting ethyl acetate was continuously distilled off. The supply of heat was continued until the distillation of ethyl acetate was complete. Afterward, the product was cooled to room temperature and dried in a vacuum for 5 h. The obtained PEOS had the following characteristics: degree of branching 0.54, SiO_2 content 49.2%, M_n 1740, and M_w/M_n 1.9 (measured by gel permeation chromatography in chloroform with evaporative light scattering detector calibrated using polystyrene standards).

N-docosane (99%) as a core element was purchased from TCI (Shanghai, China) Development Co., Ltd. Waterborne polyurethane was obtained from Shanghai Ruiqi Chemical Co., Ltd., China. Sodium bicarbonate was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Deionized water of Milli-Q grade was used for all experiments.

All chemical reagents were used without further purification. Fabrics (100 g/m², cotton 100%, plain woven) were supplied by Youngor Group Co., Ltd., Ningbo, China.

2.2. Apparatus

Field emission scanning electron microscopy (FE-SEM) was carried out by a Hitachi S-4800. Transmission electron microscopy (TEM) was carried out by a Hitachi H800. The hydrodynamic diameter of the capsules was measured with a dynamic light scattering instrument (DLS, Malvern Instruments Zetasizer Nano ZS, UK) with noninvasive back-scatter technology. Fourier transformation infrared (FTIR) spectra were obtained using a Nicolet 6700. Thermogravimetric Analysis (TGA) measurement was carried out by Netzsch STA449 F3. Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 204F1 differential scanning calorimeter. The universal testing machine from Tinius Olsen was model H5KS with a measuring accuracy of 0.5%. The thermal imaging camera with setting emissivity (ϵ) 0.90 was a FLIR E40 with infrared thermography with an accuracy of $0.05\% + 0.3\text{ }^{\circ}\text{C}$. The thermostatic plate was an ETOOL ET-150 with an accuracy of $\pm 1\sim 2\%$ $^{\circ}\text{C}$. Ultraviolet Transmittance Analysis was performed using a Labsphere UV-2000F. The reflectance spectrophotometer was a Datacolor 650, The universal testing machine was a Tinius Olsen H5KS.

2.3. Synthesis of Silica-Based Core-Shell Nanoencapsules

PCM (*n*-docosane, 0.5 g) was melted completely in hot, deionized water (60 $^{\circ}\text{C}$, 10 mL) and then PEOS (0.5 g) was added. The mixture was emulsified using ultrasonic irradiation for 15 min at 60 $^{\circ}\text{C}$ (Scientz 650E, 6 mm microtip and 1.0 time circle, 227 W output). Afterward, the resulting *o/w* emulsion was stirred gently at 60 $^{\circ}\text{C}$ for 24 h. Silica-based core-shell nanocapsules loading PCM (PCM@SiO₂) were isolated by centrifugation at 15,000 rpm for 20 min and rinsing 3 times with hot water, then re-dispersed in water or freeze-dried for further measurement. The hollow silica nanocapsules (HSNCs) were obtained by calcining the freezing-dried sample in a muffle oven at 500 $^{\circ}\text{C}$ for 2 h.

2.4. Fabrication of Functional Textile

Fabrics were incorporated with PCM@SiO₂ via a pad-dry-cure process for preparation of the functional textile. Amounts of PCM@SiO₂ (10%, 20% and 30% of the weight of fabric, labelled as FT10, FT20 and FT30) were added to the polyurethane emulsion (50 g/L) with a pH value of 7–8 adjusted by saturated NaHCO₃. The suspension was ultrasonicated for 30 min. The fabrics were dipped into this suspension and then padded (pick up of 70–80%) with a speed of 2 m/min using two dips two nips. Then, the samples were dried at 90 $^{\circ}\text{C}$ for 3 min and cured at 120 $^{\circ}\text{C}$ for 3 min.

2.5. Characterization

Field emission scanning electron microscopy (FE-SEM) with an accelerating voltage of 1.5 kV and transmission electron microscopy (TEM) with an accelerating voltage of 120 kV were used for morphological and microstructure characterization. The hydrodynamic diameter of the silica-based nanocapsules in water was measured at a scattering angle of 173 $^{\circ}$ at 25 $^{\circ}\text{C}$, after which the stock dispersions were diluted to a silica concentration of 1.0‰.

A fourier transformation infrared spectroscope (FT-IR, spectra from 400 to 4000 cm^{−1} with a resolution of 4 cm^{−1} using KBr pellets) was used to analyze the chemical compositions. The samples were vacuum-freeze-dried before measurement.

The leakage rate (*Lr*) was measured to determine leakage prevention of PCM@SiO₂. The PCM@SiO₂ samples were heated at 50 $^{\circ}\text{C}$ on filter paper for 30 min and weighed after cooling to room temperature. Before weighing, the filter paper was changed. The leakage rate was calculated by using the following Equation (1) [34]:

$$Lr(\%) = \frac{M_0 - M_t}{M_0} \times 100\% \quad (1)$$

where M_0 is initial mass and M_t is terminal mass.

Thermogravimetric Analysis (TGA) was employed to investigate the thermal stability and degradation profiles of samples under nitrogen atmosphere with a flow rate of 20 mL/min and a heating rate of 10 °C/min from room temperature to 800 °C. Differential scanning calorimetry (DSC) was conducted to characterize the latent heat-storage behaviors of samples under nitrogen atmosphere at a heating or cooling rate of 10 °C/min with a sample weight of around 5–10 mg.

The thermal regulation of the resulting functional fabrics was evaluated as follows:

The fabric samples were placed over a working heater at room temperature and a thermocouple was employed as a temperature probe to measure the temperature at above 5 cm of the top surface of the functional fabrics (Figure 1). For the heating process, plated specimens were placed on a heater and kept at a constant temperature of 40 °C. For the cooling process, specimens on a heater were heated to 40 °C and then put on a heater kept at a constant temperature of 15 °C. The thermal regulation of the resulting functional fabric was also evaluated by infrared thermography and a thermal imaging camera with an emissivity setting of (ϵ) 0.90.

Figure 1. Schematic diagram of thermal regulation performance test of functional textiles.

The anti-ultraviolet property of the fabrics was examined according to the AATCC 183-2014 by Ultraviolet Transmittance Analyzer. The Ultraviolet Protection Factor (UPF) was measured at 10 different locations before and after 10 wash cycles for each sample. The durability of the anti-ultraviolet property was evaluated by GB/T 18830, and washing requirements complied with GB/T 8629.

The universal testing machine (H5KS, Tinius Olsen, Horsham, PA, USA) was employed to measure the tensile strength of the fabric in accordance with ASTM D5035. The tested samples were cut to dimensions of 150 × 50 mm². The tensile speed rate was 300 mm/min and for every sample an average value of five replicates was adopted.

3. Results and Discussion

3.1. Preparation of Silica-Based Core-Shell Nanocapsules

The silica-based core-shell nanocapsules were synthesized under ultrasonic irradiation. The PEOS and PCM were not miscible, but a stable *o/w* miniemulsion was formed in hot water via high-energy homogenization. PEOS, as a stabilizer, collected on the surface of PCM droplets due to the amphiphilicity induced by hydrolysis of PEOS at the *oil/water* interfaces. As the polymerization continued, driven by osmotic pressure and incompatibility, PEOS molecules continuously migrated towards the *oil/water* interface where they

were consumed [35]. As soon as the polymerization was completed, the PEOS molecules were fully converted to silica on PCM droplet interfaces (Figure 2). In this system, PEOS macromolecules were only located on the surface of the PCM core because of their immiscibility with molten PCM; thus, they have much better access to water. Therefore, the PEOS conversion was completed within a short time (Figure 3). After stirring for 24 h, the PEOS was completely converted to silica matrix on the PCM surface, and silica shell was formed to produce silica-based core-shell nanocapsules (PCM@SiO₂). The products can be isolated by centrifugation and redispersed in water.

Figure 2. Illustration of formation mechanism of silica-based core-shell nanocapsules.

Figure 3. The hydrolysis and condensation reactions of PEOS for synthesis of silica shell (Et = CH₃CH₂-).

The morphology of PCM@SiO₂ was investigated by FESEM and TEM imaging. As shown in Figure 4a, monodisperse nanospheres with an average diameter of ~400 nm was observed. The polymerization was initiated after stirring the PEOS/PCM-in-water miniemulsion at 60 °C, and the thin, soft silica layer was already present at the *oil/water* interface due to the further PEOS conversion. When the reaction finished, the inner PCM and silica shells shrank as the temperature cooled, causing these particles to have wrinkled surfaces. The fragmented nanocapsules in Figure 4b indicate the core-shell structure. Moreover, the well-defined core-shell structure with an average shell thickness of about 14 nm was confirmed by TEM micrograph (Figure 4c).

Figure 4. Electron micrographs of (a) silica-based nanocapsules by FE-SEM, (b) broken capsules by FE-SEM, (c) by TEM.

The chemical composition of the product was further identified via FT-IR spectroscopy. Figure 5 shows the FT-IR spectra of pure PEOS, PCM, dried PCM@SiO₂ and HSNCs obtained after calcination. In the spectra of PCM@SiO₂, the characteristic bands at 1100 cm⁻¹, 800 cm⁻¹ and 470 cm⁻¹ were attributed to Si-O-Si and Si-O of silica shells and the absorption bands of C-H at 2930 cm⁻¹ and 1470 cm⁻¹ were attributed to the PCM core. The spectrum of the core-shell particles appears to be a superposition of the spectra of PCM and the hollow spheres consisting entirely of pure silica, indicating the full conversion of PEOS to silica and the successful encapsulation of PCM. Thus, this self-assembly method via miniemulsion based on hyperbranched polyethoxysiloxane (PEOS) for preparing silica-encapsulating PCM was easy, efficient, and economically feasible.

Figure 5. FTIR spectra of PCM, PEOS, hollow silica nanocapsules (HSNCs) and silica-based core-shell nanocapsules (PCM@SiO₂).

3.2. Thermal Stability of Silica-Based Core-Shell Nanocapsules

The thermal stability and encapsulation capability of the nanocapsules are critical to performance, especially if they are utilized in situations where thermal regulation is necessary. From Figure 6 of TGA, the major differences between PCM, PCM@SiO₂ and HSNCs were weight-loss steps and residual mass. It was a classical one-step weight loss of PCM, there was nothing remaining after heating to 800 °C, and the temperature of onset degradation and maximum decomposition rate for PCM were 162.29 °C and 233.42 °C, respectively. However, approximately 30% residual mass of PCM@SiO₂ remained, with two weight-loss stages and almost 95% residual mass for HSNCs with one-step weight loss. There was a trivial 5% weight loss at 138 °C, attributed to the removal of humid water and loss of the loosely bonded absorbed water on the surface of silica nanocapsules for both PCM@SiO₂ and HSNCs. The weight loss of PCM@SiO₂ not only corresponded to the evaporation of water from silica shells, but also degradation of PCM in the microcapsules at approximately 200 °C. It could be deduced that about 65% PCM was encapsulated [36]. Moreover, the initial degradation temperature of PCM@SiO₂ was higher than that of pristine PCM, indicating that the inert silica shell could act as protective layer of the inner PCM, and the thermal stability was markedly improved. Meanwhile, it was surprising that silica, as inorganic shells of the nanocapsules, retained its original morphological structure even after being calcinated at 500 °C for 2 h. It would eliminate the encapsulated PCM leakage at high-temperature, and significantly increase the range of its applications. The leakage rate of PCM@SiO₂ was 2.57%. Compared with pristine PCM without silica shells, the leakage rate of PCM@SiO₂ decreased by 89.33%. This was due to the silica shell layer obstructing the leakage of PCM, suggesting good structural stability and barrier efficiency of the silica shells.

Figure 6. TGA curves of PCM, HSCNs and PCM@SiO₂.

3.3. Thermal Performance of Silica-Based Core-Shell Nanocapsules

Thermal performance, latent thermal energy storage and release by PCM@SiO₂ can be related to the enthalpy change during melting and cooling, measured and investigated via DSC. Figure 7 and Table 1 show the DSC results of PCM and PCM@SiO₂.

Figure 7. Crystallizing (a) and melting (b) DSC curves of PCM and PCM@SiO₂.

Table 1. Phase change properties of PCM and PCM@SiO₂.

	T_m (°C)	T_s (°C)	ΔH_m (%)	ΔH_s (%)	Er (%)	Ee (%)
PCM@SiO ₂	28.7	22.7	126.2	123.4	60.2	59.2
PCM	29.5	25.5	209.5	211.8		

T_m and T_s , the peak temperatures indicating melting and solid states, respectively. ΔH_m and ΔH_s , the melting and solidified enthalpies, respectively. Er represents the encapsulation ratio, Ee represents the encapsulation efficiency, and these can be calculated by Equations (2) and (3), respectively.

On the DSC curve of PCM and PCM@SiO₂ obtained during cooling, exothermic peaks occur at 25.5 °C and 22.7 °C, and during melting endothermic peaks at 29.5 °C and 28.7 °C. The exothermic and endothermic peaks of nanoencapsulated PCM are lower and narrower than that of pure PCM. The T_s and T_m of PCM@SiO₂ were slightly decreased by 2.8 °C and 0.8 °C, respectively. The change in the phase transition temperature can be ascribed to the reaction between PCM and the silica shells, as well as the confined effect of nanocapsules [37]. The phase transition temperature and latent heat (phase transition enthalpies) of them are summarized in Table 1. It can be seen that the enthalpy of PCM@SiO₂, which only considered the PCM encapsulated within the silica nanocapsules, was lower than that of free PCM, and that cooling enthalpies were below those of melting. The free PCM had a ΔH_s of 211.8 J/g and ΔH_m of 209.5 J/g. In contrast the ΔH_s and ΔH_m of PCM@SiO₂ were 123.4 J/g and 126.2 J/g, respectively.

Encapsulation ratio (Er) and encapsulation efficiency (Ee) are important parameters in studying heat energy storage and thermal regulation, which represented the effective

performance of the PCM inside the silica nanocapsules. Er and Ee were calculated from the values of enthalpy of PCM@SiO₂ by using Equations (2) and (3) [38]:

$$Er(\%) = \frac{\Delta H_{m \text{ encapsulated PCM}}}{\Delta H_{m \text{ free PCM}}} \times 100\% \quad (2)$$

$$Ee(\%) = \frac{\Delta H_{m \text{ encapsulated PCM}} + \Delta H_{c \text{ encapsulated PCM}}}{\Delta H_{m \text{ free PCM}} + \Delta H_{c \text{ free PCM}}} \times 100\% \quad (3)$$

where ΔH_m and ΔH_c are melting enthalpy and crystallization, respectively. The results were consistent with the investigation by TGA.

3.4. Functional Textile with Silica-Based Core-Shell Nanocapsules

3.4.1. Morphology of Functional Textile

Surface morphologies of functional fabric with PCM@SiO₂ are shown in Figure 8, revealing the morphologies of the functional textile. PCM@SiO₂ assembly exhibited random distribution on the fiber surface of the fabric. The PCM@SiO₂ layer on fabric was increasingly dense with increasing applied amounts of PCM@SiO₂. From the insets of Figure 8, the functional textile had no obvious changes after 10 wash cycles compared to the unwashed samples. It implies that the functional textile shows greater durability during washing.

Figure 8. FESEM images of (a–c) original fabric at 100, 1000, 3000 magnifications, respectively, (d–f) FT10 at 100, 1000, 3000 magnifications, respectively, (g–i) FT20 at 100, 1000, 3000 magnifications, respectively, (j–l) FT30 at 100, 1000, 3000 magnifications, respectively, and the insets show the corresponding FESEM images of functional textile after 10 wash cycles at 100, 1000, 3000, respectively.

3.4.2. Thermal Regulation of Functional Textile

The thermoregulation properties of a functional textile with PCM@SiO₂ was characterized by DSC and thermal measurement. As shown in Figure 9, the T_m and T_c of the functional textile were almost identical with that of PCM@SiO₂. Latent heat, characteristic of the amount of stored energy during phase change, was determined. The latent heat (enthalpies) of the functional textile increased for both heating and cooling processes with increasing PCM@SiO₂ incorporation, indicating that it was dependent on the content of PCM encapsulated. PCM@SiO₂ exhibited a high storage capacity of thermal energy. The latent heat of melting and crystallizing were measured to be 5.6 J/g and 5.3 J/g for FT10, 14.2 J/g and 14.3 J/g for FT20, 27.7 J/g and 27.8 J/g for FT30, respectively. Although latent heat (enthalpies) of the functional textile decreased a little after 10 washed cycles (ascribed to loosely attached capsules being expelled during washing), its excellent energy storage/release properties remained. These results indicated that the functional textile with PCM@SiO₂ exhibited advantages in thermal regulation.

Figure 9. DSC curves of functional textile during (a) cooling and (b) heating processes. (Solid curves represent functional textile before washed cycles. Dashed curves represent functional textile after 10 washed cycles).

The thermoregulation performance of the functional textile with PCM@SiO₂ was investigated during the heating and cooling processes, and the temperature–time diagrams obtained along are illustrated in Figure 10, in which the relevant data for the original fabric is also presented. It was observed from these two diagrams that the temperature of the original fabric experiences a continuous elevation during heating, with an increase in heating time, and then decreases without any hysteresis during the cooling stage. With the functional textile, in contrast, temperature hysteresis was close to the phase-change temperature ranges of PCM@SiO₂, attributed to the amount of absorbed or released latent heat of the encapsulated PCM in the melting or crystallizing processes with increasing or decreasing temperature, indicating that the functional textile possessed excellent thermoregulation and thermal-management performance. In the inset thermographic images, the target color was considered as a temperature indicator, and it clearly indicated that the temperature of the functional textile was lower than that of the original fabric in the heating process, but higher than that of the original one during the cooling stage due to their thermoregulatory capability. Although it was lower, the thermal regulation of the functional textile with PCM@SiO₂ after washing still showed excellent thermoregulation performance. All the results clearly proved that the functional textile with PCM@SiO₂ developed by this investigation had a good thermoregulatory capability to perform effective thermal management for potential applications in many fields, such as smart temperature-regulated garments and interior energy-saving decorative fabrics.

Figure 10. Time-dependent changes in surface temperature of functional textile under heating (a) and cooling (b) processes. Solid curves represent functional fabric before washing cycles. Dashed curves represent functional fabric after 10 washing cycles. (Green: original fabric, Black: FT10, Red: FT20, Blue: FT30; the relevant thermographic images of original fabric and FT30 were inserted.).

3.4.3. Anti-Ultraviolet and Mechanical Properties of Functional Textile

The UPF values of all functional textiles with PCM@SiO₂ before and after washing are shown in Figure 11. The UPF value of the original fabric was only 14.50. The UPF value of blank (fabric treated with PU) was 16.53, showing a small increase in anti-ultraviolet capability, but was not sufficient to provide UV protection. The PCM@SiO₂ covering on fabrics was noticeably effective at increasing UV resistance; the UPF values were 27.22 for FT10, 52.94 for FT20 and 77.85 (in Table 2) for FT30, implying a potential function of the textile as anti-ultraviolet protection. The silica nanocapsules on the functional textile played a major role in reflecting UV light and displayed excellent anti-ultraviolet properties [39]. To assess the durability of the anti-ultraviolet property of the functional textile, the samples were washed over 10 cycles, after which the UPF was measured. The light reduction in the UPF value indicates excellent durability due to the silica-based nanoencapsulated PCM binding tightly to the fabrics.

Figure 11. The anti-ultraviolet performance of functional textile and durability.

Table 2. Anti-ultraviolet and mechanical properties of functional textile.

Samples	UPF		Tensile Strength (N)	
	Before Washing	After Washing	Warp	Weft
Original	14.50 ± 2.37		502.0 ± 8.9	227.6 ± 7.8
Blank ^a	16.53 ± 2.13	16.37 ± 1.89	496.7 ± 10.3	220.2 ± 11.6
FT10	27.11 ± 1.34	24.47 ± 3.23	509.7 ± 7.4	257.6 ± 5.4
FT20	52.94 ± 2.17	48.58 ± 1.11	538.4 ± 6.9	267.7 ± 3.3
FT30	77.85 ± 4.20	61.39 ± 4.98	545.2 ± 11.7	290.5 ± 10.4

^a Fabric treated with 50 g/L of pure WPU.

In Table 2, the tensile strength of functional textiles with different PCM@SiO₂ contents is displayed. The tensile strength of functional textiles increases with greater amounts of PCM@SiO₂ on the fabric. There might be two reasons for the increased tensile strength of the functional textile: the PCM@SiO₂ hybrid layer may cover fibers to strengthen the fabric, or it may construct more compact crosslinking networks among the fibers [40]. Interpenetrating the composite PCM@SiO₂ and polymers in the fabric could dissipate energy under tensile pressure and improve the mechanical properties of the textile.

4. Conclusions

In this work, silica-based core-shell nanocapsules loaded with PCM (PCM@SiO₂) were synthesized with a silica precursor polymer as well as emulsion stabilizer-hyperbranched polyethoxysiloxane (PEOS) through a self-assembly method in a surfactant-free miniemulsion approach. The morphology, chemical structures, thermal stability and latent thermal energy storage of PCM@SiO₂ were confirmed by FESEM, TEM, FTIR, TGA and DSC. The obtained silica-based core-shell consisted of nanocapsules with diameters of ~400 nm and silica shells of ~35 nm, and reached the maximum PCM core content of 65%. The silica shell had basically no significant influence on the phase change behavior of PCM, while the PCM@SiO₂ exhibited a high melting enthalpy and crystallization of 123–126 J/g.

A novel textile with added PCM@SiO₂ has been proposed with the aim to develop functional textiles with thermal regulation and UV resistance to be utilized for energy-saving and thermal comfort. The functional textile was systematically analyzed. With the increasing amount of PCM@SiO₂ in the fabrics, the latent heat of melting and crystallizing in DSC of the functional textile rose, as well as, increasingly, the anti-ultraviolet. The functional textile with a PCM@SiO₂ concentration of 30% was promising, with the melting enthalpies and crystallization of 27.7 J/g and 27.8 J/g, respectively, and UV resistance of 77.85. The

temperature hysteresis was studied by infrared thermography. These fabrics could be potentially used for thermal comfort, protective and energy-saving textile applications. The experiment demonstrated the durability of thermal regulation and UV protection properties in the functional textile after being rinsed.

Accordingly, we believe that this study has proposed a versatile method to fabricate a novel functional textile with combined thermal energy storage, UV resistance and comfort. It indicated that the silica-based core-shell nanocapsules could hold potential for multifunctional textiles.

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