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Research Article

Preparation and Characterization of Double-Layered Microcapsules Containing Nano-SiO_2

Xue Sun, Jingcheng Su, Rui Zhang, and Fangyu Fan

Key Laboratory for Forest Resources Conservation and Utilisation in the Southwest Mountains of China, Ministry of Education, and College of Life Sciences, Southwest Forestry University, Kunming, Yunnan 650224, China

Correspondence should be addressed to Fangyu Fan; ffy118@163.com

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The double-layered microencapsulation technology has been used in many fields. In this study, the double-layered microencapsulated anthocyanin of *Passiflora edulis* shells (APESs) was prepared via complex coacervation using gelatin and gum Arabic as the first wall materials (single-layered microcapsules (SMs)) and using gum Arabic containing nano-SiO_2 as the second wall material (double-layered microcapsules (DMs)/nano-SiO_2) to enhance the stability of the core material. Properties of microcapsules were analyzed on the basis of EE, morphology, scanning electron microscopy (SEM), droplet size, moisture content, and differential scanning calorimetry (DSC). The results showed that the EE values of SMs, DMs, and DMs/nano-SiO_2 were 96.12%, 97.24%, and 97.85%, respectively. DMs/nano-SiO_2 had the lowest moisture content (2.17%). The average droplet size of DMs/nano-SiO_2 (34.93 μm) was higher than those of SMs and DMs. DSC indicated that the melting temperature of DMs/nano-SiO_2 was 73.61°C and 45.33°C higher than those of SMs and DMs, respectively. SEM demonstrated that DMs/nano-SiO_2 had the smoothest surface compared with the other two kinds of microcapsules. The storage stability of APESs and their microcapsules indicated that the stability of the microcapsules was improved by adding DMs/nano-SiO_2 into the wall material of microcapsules. These results indicated double-layered microcapsules containing silica nanoparticles contribute to the stability of the core material.

1. Introduction

Microencapsulation technology is often applied to encapsulate unstable substances in the food industry, including oils [1], vitamins [2], and probiotics [3]. The protective layer of microcapsules prevented adverse conditions from affecting core materials, such as temperature, humidity, oxidation, and light [4]. The complex coacervation method, a microencapsulation technology, forms microcapsules via the electrostatic action from a mixture of two polymers with opposite charges. Tiebackx [5] first proposed the formation process of complex coacervation microcapsules, and Overbeek and Voorn [6] established the model of the complex coacervation process. Proteins and polysaccharides are used as wall materials during the preparation of microcapsules by complex coacervation [7]. Gelatin and gum Arabic are commonly selected to prepare microcapsules by complex coacervation because of the slow release of the core material of microcapsules. Microcapsules containing anthocyanins [8], curcuminoid [9], tuna oil [10], flaxseed oil [11], and bacteria [12] are successfully prepared using gelatin and gum Arabic in many fields.

According to previous studies, core materials of single-layered microcapsules (SMs) are easily destroyed during storage at high temperature, high humidity, or light [13]. The reason is that single-layered microcapsules have some drawbacks, such as unsatisfied release characteristics and low payload [14]. For protecting unstable compounds, the double-embedding technology can change the droplet characteristics, such as wall thickness, permeability, and environmental responsiveness, which influence the release characteristic of microcapsules. Previous studies have indicated that double-layered microcapsules (DMs) are more stable than SMs [15, 16]. Sun et al. [17] have improved the stability of microcapsules by preparing DMs. Fioramonti et al. [13] have prepared the double-layered flaxseed oil microcapsules of whey

protein and sodium alginate, and improved the encapsulation efficiency (EE) of microcapsules. Therefore, improving the properties of the wall material and maintaining the stability of the core material are always the research focus of DMs.

In recent years, nanoparticles are used to improve the mechanical and gas barrier properties of macromolecular materials because of their particle size, large surface area, high surface energy, unsaturated chemical bonds, surface hydroxyl, and dispersibility in an aqueous solution [18]; their products can control the release properties of carriers and enhance the thermal stability [19, 20]. Hou et al. [21] have prepared the agar/sodium alginate/nano-SiO_2 film that improves the mechanical properties, water resistance, and thermal stability of nanocomposite films. Ergun et al. [22] have found that the mechanical properties of the poly(methyl methacrylate) increased with increasing nano-ZrO_2 content ranging from 5% to 20%. Based on the advantages of modifications, microcapsules with nanomaterial wall materials are prepared, and good results are achieved. Leroux et al. [23] have reported a new type of microcapsule with TiO_2-modified sodium alginate wall material. Chen et al. [24] have prepared fluoroalkyl silane- (FAS-) loaded polystyrene microcapsules via the Pickering emulsion techniques. Zhang et al. [25] have indicated that the release rate of FAS depends on the content of nano-SiO_2/TiO_2. Among nanoparticles, nano-SiO_2 is the most widely used due to availability and low cost compared with other nanoparticles.

To the best of our knowledge, there are few reports about the application of microcapsules containing nano-SiO_2 in the food industry. This study prepared DMs by gum Arabic containing nano-SiO_2. The core material was the anthocyanins of *Passiflora edulis* shells (APESs) [26]. Anthocyanins have attracted considerable attention due to their physiological activities, such as antioxidant and anticarcinogenic activities [27, 28], but their stability is poor.

In this study, anthocyanin microcapsules were prepared using the double-layered embedding technique. Gelatin and gum Arabic were selected as the first wall materials, and gum Arabic containing nano-SiO_2 was used as the second wall material to prepare microcapsules. The properties of microcapsules were analyzed on the basis of EE, morphology, scanning electron microscopy (SEM), droplet size, moisture content, and differential scanning calorimetry (DSC). Moreover, the stability of anthocyanin microcapsules was analyzed in the presence of light, different storage temperatures (4°C, 20°C, 40°C, and 60°C), and different relative humidities (11%, 33%, 53%, and 75%).

2. Materials and Methods

2.1. Materials. Gelatin and gum Arabic were purchased from China Medicine (Group) Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Transglutaminase (TGase) was obtained from Taixing Zhengjiang Food Science & Technology Co., Ltd. (Zhengjiang, China). Sodium dodecyl sulfonate (SDS) was purchased from the Tianjin Bailunsi Biotechnology Co., Ltd. (Tianjin, China). Nano-SiO_2 (20–30 nm) was obtained from Zhoushan Mingri Co., Ltd. (Zhejiang, China). The APESs were extracted from the *Passiflora edulis* grown in Kunming, Yunnan, China, and stored at -18°C. All chemical reagents were of analytical grade or pure.

2.2. Methods

2.2.1. Preparation of SMs. SMs were prepared using the complex coacervation method. Gelatin and gum Arabic solutions were prepared by dissolving 1.5 g gelatin and gum Arabic into 100 mL distilled water (40°C), respectively. Subsequently, APESs (0.6 g) were added into the gelatin solution and homogenized using a high-speed disperser (FUXI, FJ200, China) under 10,000 rpm at 25°C for 30 min. The gum Arabic solution was added into the mixture solution. The pH of the mixture was adjusted to 3.5 with 10% glacial acetic acid, and the mixture was stirred under 200 rpm at 40°C for 30 min. The solution was cooled to 15°C, and TGase was added to solidify the microcapsules under 200 rpm at 15°C for 3 h. Finally, SMs were obtained by spray drying. The operation conditions for the spray dryer (B-290, Buchi, Switzerland) were as follows: liquid flow rate—9 mL/min; inlet air temperature—180°C; and outlet air temperature—90°C.

2.2.2. Activation of Nano-SiO_2. The nano-SiO_2 was activated before addition to the wall materials of DMs. Nano-SiO_2 (5 g) was added into 1000 mL of 0.7% SDS solution. The pH was adjusted to 4.0 by using 1 mol/L sodium hydroxide and stirred at 80°C for 6 h. Then, the nano-SiO_2 was washed with deionized water by repeated centrifugations at 5500 rpm and dried at 55°C for 12 h.

2.2.3. Preparation of DMs. DMs were prepared using gum Arabic as the second wall material. Microcapsules were prepared as follows. Gum Arabic (100 mL, 6%) and SM (100 mL) solutions were mixed using an agitator (AICE, JJ-1, China) under 200 rpm at 25°C for 30 min. DMs were obtained by spray drying. The spray drying conditions were the same as those in Section 2.2.1.

2.2.4. Preparation of DMs Containing Nano-SiO_2. DMs containing nano-SiO_2 (DMs/nano-SiO_2) were prepared by adding nano-SiO_2 to the second wall material of the microcapsule as a protective layer. DMs were prepared as follows. The nano-SiO_2 dispersion was obtained by adding 0.15 g of nano-SiO_2 into 100 mL distilled water, and an ultrasonic processor (JRA-650, China) was used to disperse the solution under 650 W for 2 h. Then, 6 g of gum Arabic was added to the nano-SiO_2 solution. The solution was stirred at 500 rpm for 30 min, and mixed with 100 mL SM solution by using an agitator (AICE, JJ-1, China) under 200 rpm at 25°C for 30 min. Finally, DMs/nano-SiO_2 was obtained by spray drying. The spray drying conditions were the same as those in Section 2.2.1.

2.2.5. EE. The total anthocyanin content (TAC) was determined in accordance with the following previous publication with some modifications [29]. The microcapsule powder (0.50 g) was dissolved in 15 mL distilled water, and the wall material of microcapsules was destroyed using an ultrasonic processor (JRA-650, China). The solution was shaken repeatedly and filtered after 30 min using a Whatman filter. The

filtrate was diluted four times by hydrochloric acid-citric acid buffer solution at pH 1.0 and citric acid-sodium citrate buffer solution at pH 4.5. The reaction was done in dark conditions for 30 min, and the absorbance values of different pH samples at 510 and 700 nm were measured by a UV spectrophotometer. The TAC (mg/100 g) was calculated as follows [29]:

$$\text{TAC} = \frac{\Delta A \times V \times \text{DF} \times M \times 100}{\varepsilon \times 1 \times m}, \quad (1)$$

where ΔA is the difference of absorbance value $((A_{532} - A_{700})_{\text{pH 1.0}} - (A_{532} - A_{700})_{\text{pH 4.5}})$, V is the dilution volume (15 mL), DF is the dilution rate (4), M is the molecular weight of cyanidin-3-glucoside (449.2 g/mol), ε is the molar extinction coefficient of cyanidin-3-glucoside (26,900), 1 is the path length of the cuvette (cm), and m is the sample weight (g).

The surface anthocyanin content (SAC) was determined as follows. The microcapsule powder (0.50 g) was immersed in 15 mL of 70% ethanol. The solution was vibrated repeatedly and filtered through a Whatman filter. The content of anthocyanin in the filtrate was determined using the same method as TAC.

The EE of microcapsules was calculated as follows:

$$\text{EE}\,(\%) = \frac{\text{TAC} - \text{SAC}}{\text{TAC}} \times 100. \quad (2)$$

2.2.6. Moisture Content. The moisture content of microcapsules was determined by the gravimetric method [30].

2.2.7. Morphology. A light microscope (SK2009P, Shenzhen, China) with the S-EYE software (1.4.7.645) was used to evaluate the morphology of microcapsules before drying. SEM (HITACHI, SC-4800, Japan) was used to analyze the microstructure of the microcapsule powder.

2.2.8. DSC Analysis. The thermal property of microcapsules was determined using a differential thermal scanner (Netzsch, DSC204, Germany) under a nitrogen atmosphere at 10°C/min from 25°C to 200°C [31]. The sample (5 mg) was placed into a sample pan of the DSC equipment, and an empty pan was used as the reference.

2.2.9. Storage Stability. The APESs and their microcapsules (i.e., SMs, DMs, and DMs/nano-SiO_2) were stored to evaluate stability in different environmental conditions, including different temperatures (4°C, 20°C, 40°C, and 60°C), different relative humidities (11%, 33%, 53%, and 75%), and light. The samples were stored for 64 d, and the anthocyanin content was measured every 8 d. The degradation kinetics of anthocyanin was analyzed using the first-order reaction kinetic model during storage [32]. Degradation parameters, including k and $t_{1/2}$, were obtained using Equations (3) and (4) [32], respectively:

$$k = \frac{\ln\,(C_t/C_0)}{t}, \quad (3)$$

$$t_{1/2} = \frac{\ln 0.5}{k}, \quad (4)$$

where C_0 is the initial anthocyanin content (mg/100 g), C_t is the anthocyanin content after time t (mg/100 g), k is the first-order kinetic constant, and $t_{1/2}$ is the half-life.

3. Results and Discussion

3.1. EE. EE is an important parameter to evaluate the quality of microcapsules, and it indicates the amount of the total core material that is actually efficiently encapsulated [33]. The stability of the microencapsulated anthocyanins is good, which can avoid the oxidation of anthocyanins exposed to the air [34]. In this study, anthocyanin microcapsules were prepared using several embedding techniques. Figure 1 shows that the EE values of SMs, DMs, and DMs/nano-SiO_2 were 96.12%, 97.24%, and 97.85%, respectively. The results showed that the double-embedding technology increased EE compared with the single-microcapsule technology especially when nano-SiO_2 was added to the wall material of microcapsules. Similar results were obtained by Fioramonti et al. [13] who prepared the double-layered flaxseed oil microcapsules of whey protein and sodium alginate. The reason is that the strong hydrogen bond and van der Waals force between nano-SiO_2 and gum Arabic make the wall structure of a microcapsule compact, not easy to break, and the core material is stable [35].

3.2. Moisture Content. The moisture content is an important factor to evaluate the shelf life of powders. Figure 2 shows that the moisture content of SMs, DMs, and DMs/nano-SiO_2 were 2.69%, 4.65%, and 2.17%, respectively. The moisture content of DMs was higher than 4.0%, the minimum specification for many powders for food applications [36]. DMs/nano-SiO_2 had the lowest moisture content (2.17%), favoring the storage of microcapsules [37]. These differences were influenced by the water-binding capacity of the different materials [38]. Nano-SiO_2 formed hydrogen bonds with the hydrophilic groups of gum Arabic, which reduced the contact between water molecules and hydrophilic groups.

3.3. Morphology. As shown in Figure 3, microcapsules were spherical with clear walls. The average droplet sizes of SMs, DMs, and DMs/nano-SiO_2 measured using the S-EYE 1.4.7.645 software were 34.03, 34.73, and 34.93 μm, respectively. The average droplet size of DMs/nano-SiO_2 was higher than those of SMs and DMs. According to relevant reports, the thickness of the composite film is affected by the addition of nanoparticles [18, 21, 39]. Therefore, the difference of droplet size is attributed to the addition of nano-SiO_2, which affected the thickness of the wall material of the microcapsule and resulted in a larger droplet size. The improvement of the wall thickness can enhance the strength and the EE of microcapsules, which had a positive effect on the stability of the microcapsules.

The SEM images of SMs, DMs, and DMs/nano-SiO_2 are presented in Figure 4. As shown in Figure 4(a) (SMs), many dents and wrinkles were observed because of the rapid evaporation of water in the microcapsule which caused uneven

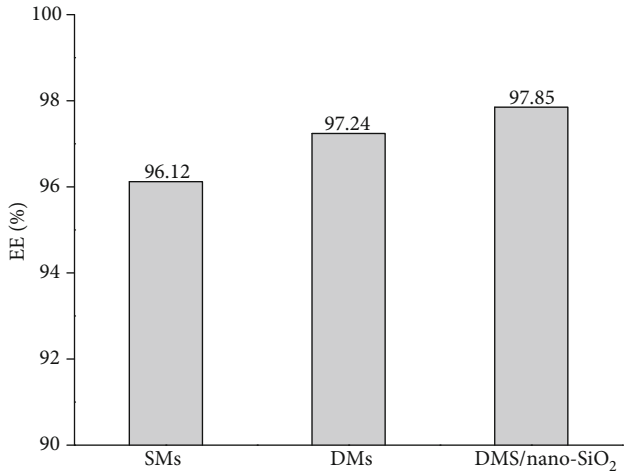

Figure 1: Encapsulation efficiency of SMs, DMs and DMs/nano-SiO_2.

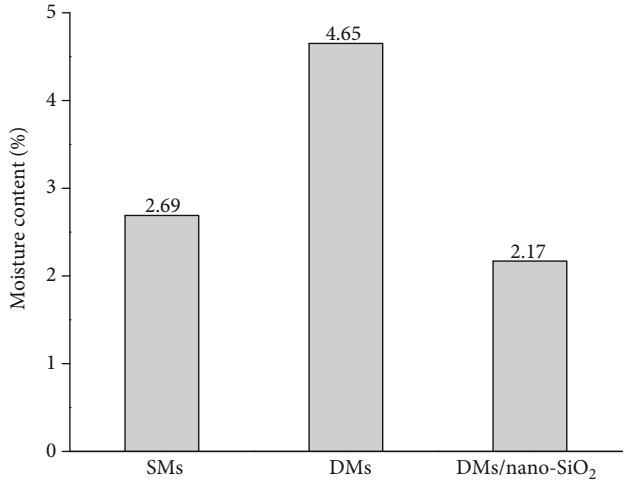

Figure 2: The moisture contents of SMs, DMs, and DMs/nano-SiO_2.

shrinkage of the wall materials during the spray drying process [36]. In Figures 4(b) and 4(c), the damage observed during spray drying is reduced, and the wrinkles of DMs and DMs/nano SiO_2 are reduced due to the protective effect of the gum Arabic layer. Compared with the two other kinds of microcapsules, DMs/nano-SiO_2 had the smoothest surface. The results indicated that nano-SiO_2 can keep the structural integrity of the microcapsules. Similar results were found in the research of Niu et al. [40]. The micrographs also showed that pores and cracks were not present on the surface of the microcapsules, which contributed to the protection of the core material by decreasing oxygen diffusion into the microcapsules [34]. In addition, some little pellets were shown in the SEM images. This phenomenon is attributed to the wall materials of microcapsules, which did not occur during the complex coacervation reaction. Some large microcapsules are attributed to secondary nucleation that is inevitable.

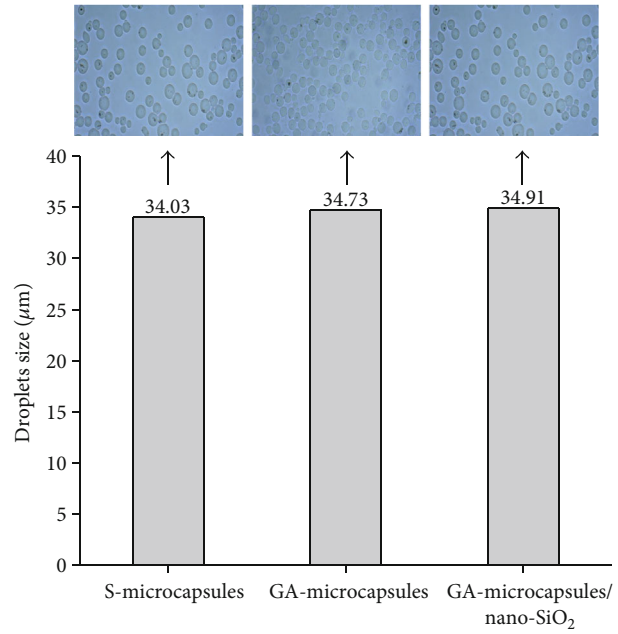

Figure 3: Droplet sizes of SMs, DMs, and DMs/nano-SiO_2 and the corresponding droplet images.

3.4. DSC Analysis. Figure 5 shows the thermal stability of SMs, DMs, and DMs/nano-SiO_2 by DSC. The melting temperatures (T_m) of SMs, DMs, and DMs/nano-SiO_2 were 82.51°C, 127.84°C, and 156.12°C, respectively. The T_m of DMs/nano-SiO_2 were 73.61°C and 45.33°C higher than those of SMs and DMs, respectively. The results showed that the stability of the microcapsules can be improved using the double-layered microcapsule technology especially when nano-SiO_2 was added to the wall material of microcapsules. Similar results were obtained by Sun et al. [17] who fabricated hexamethylene diisocyanate-filled double-walled polyurea microcapsules with excellent resistance to the thermal environment because the hydrogen bond and van der Waals force between nano-SiO_2 and gum Arabic are produced. These bond energies need high external energy to be destroyed. The improvement of thermal stability can play a positive role in the storage of core materials.

3.5. Storage Stability. The storage stability of APESs and their microcapsules was studied under different conditions (i.e., light, temperature, and relative humidity), and the degradation kinetics was evaluated by the first-order reaction kinetic. Table 1 and Figure 6 show that the degradation of APESs and their microcapsules followed the first-order reaction kinetic. The correlation coefficients (R^2) were greater than 0.92, and the results were in agreement with the other reports [32, 41, 42].

Table 1 and Figure 6(a) show that the degradation rate of APESs was faster than those of their microcapsules in the presence of light. The half-life ($t_{1/2}$) values of APESs, SMs, DMs, and DMs/nano-SiO_2 were 44.34, 82.24, 112.75, and 128.73 d, respectively. The results revealed that the microencapsulation of APESs delays the degradation rate. The $t_{1/2}$ of

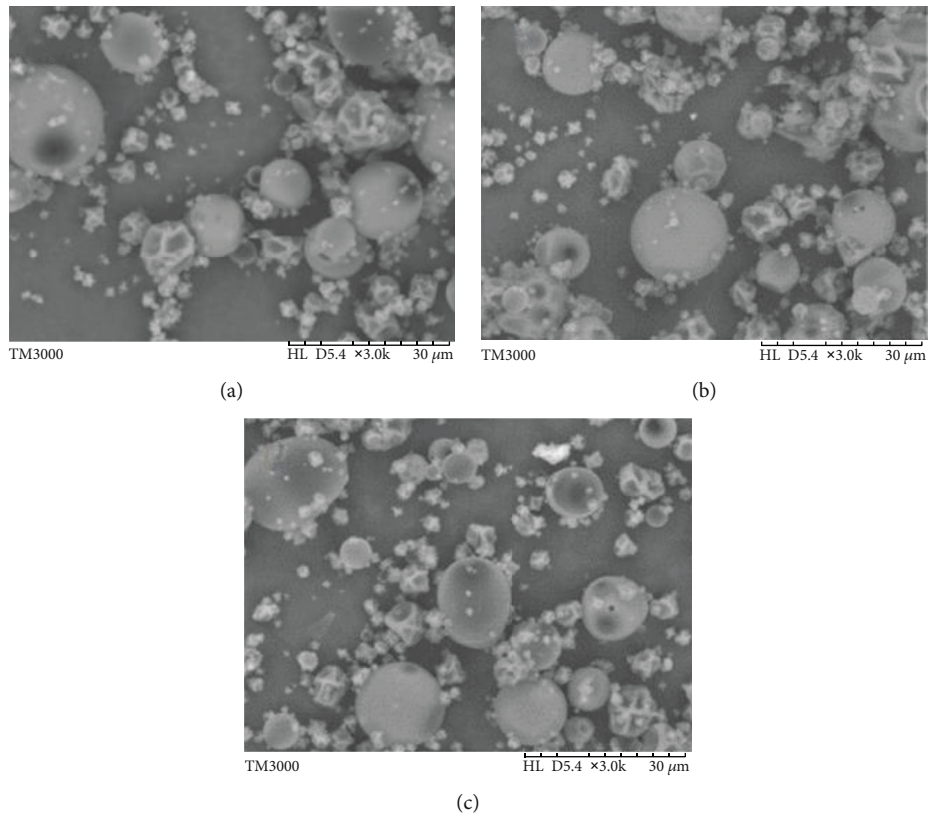

Figure 4: The SEM pictures of SMs (a), DMs (b) and DMs/nano-SiO_2 (c).

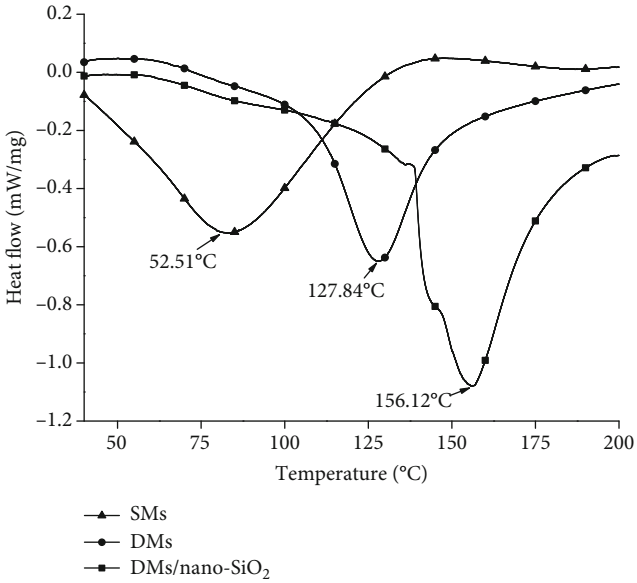

Figure 5: The DSC curves of SMs, DMs, and DMs/nano-SiO_2.

DMs/nano-SiO_2 was 14.18% higher than that of DMs. The difference in $t_{1/2}$ was attributed to the addition of nano-SiO_2 that affects the wall material structure of microcapsules, thereby protecting APESs from external light and delaying the damage of light to anthocyanins.

The temperature influences the stability of anthocyanin and its microcapsules (Table 1 and Figures 6(b)–6(e)). The $t_{1/2}$ values of APESs, SMs, DMs, and DMS/nano-SiO_2 stored at 4°C were 193.28, 255.56, 368.98, and 627.27 d, respectively. The $t_{1/2}$ values of APESs, SMs, and DMs were shortened by 69.19%, 59.26%, and 41.22%, respectively, compared with DMS/nano-SiO_2 at 4°C. The results indicated that nano-SiO_2 can improve the stability of a microcapsule, which was consistent with the DSC results in Section 3.4. According to reports of Xu et al. [43], the addition of nano-SiO_2 to the composite film resulted in the improvement of mechanical properties because of the formation of the network structure between nano-SiO_2 and the SPI matrix. In this study, the storage stability of DMS/nano-SiO_2 was significantly ($p < 0.05$) higher than those of the three other groups (i.e., APESs, SMs, and DMs), which is due to the addition of nano-SiO_2 that improved the mechanical properties of the microcapsule wall materials. The core material (i.e., anthocyanin) was covered with the wall materials of microcapsules, which resulted in the improved storage stability of anthocyanin. The storage stability of DMS/nano-SiO_2 at different temperatures showed that the $t_{1/2}$ value was 627.27 d at 4°C, which was 549.32 d longer than that at 60°C. The results indicated that a high temperature was not beneficial to the storage of anthocyanin, which may be attributed to the effects of temperatures on the structure of anthocyanin [44].

Table 1: Reaction constant (k), determination coefficients (R^2), and half-life ($t_{1/2}$) under different storage conditions.

Storage conditions		Light	Temperature (°C)				Relative humidity (%)			
			4	20	40	60	11	33	53	75
APESs	$k \times 10^3$ (d^{-1})	15.56 ± 0.61^a	3.57 ± 0.21^a	7.89 ± 0.46^a	12.35 ± 0.72^a	14.96 ± 0.80^a	3.72 ± 0.19^a	4.98 ± 0.33^a	8.02 ± 0.38^a	10.09 ± 0.45^a
	R^2	0.9892	0.9754	0.9770	0.9767	0.9774	0.9822	0.9707	0.9845	0.9842
	$t_{1/2}$ (d)	44.34	193.28	87.45	55.87	46.32	184.99	138.55	86.03	68.68
SMs	$k \times 10^3$ (d^{-1})	8.39 ± 0.88^b	2.7 ± 0.17^b	5.88 ± 0.27^b	8.50 ± 0.55^b	10.99 ± 0.58^b	3.12 ± 0.20^b	3.55 ± 0.32^b	6.49 ± 0.69^b	8.28 ± 0.66^b
	R^2	0.9280	0.9721	0.9859	0.9710	0.9785	0.9707	0.9477	0.9266	0.9511
	$t_{1/2}$ (d)	82.24	255.56	117.35	81.18	63.06	221.15	194.37	96.32	83.70
DMs	$k \times 10^3$ (d^{-1})	6.12 ± 0.76^c	1.87 ± 0.14^c	5.33 ± 0.25^{bc}	6.03 ± 0.23^c	9.04 ± 0.52	2.74 ± 0.19^c	3.33 ± 0.16^b	6.86 ± 0.59^b	7.86 ± 0.48^b
	R^2	0.9016	0.9620	0.9853	0.9901	0.9739	0.9674	0.9850	0.9500	0.9713
	$t_{1/2}$ (d)	112.75	368.98	129.46	114.43	76.66	251.82	207.21	100.58	88.17
DMs/nano-SiO_2	$k \times 10^3$ (d^{-1})	5.36 ± 0.42^c	1.10 ± 0.04^d	5.03 ± 0.32^d	5.93 ± 0.15^c	8.89 ± 0.74^c	2.72 ± 0.33^c	3.25 ± 0.23^b	6.39 ± 0.32^b	7.63 ± 0.46^b
	R^2	0.9596	0.9921	0.9730	0.9953	0.9465	0.9061	0.9671	0.9827	0.9721
	$t_{1/2}$ (d)	128.73	627.27	137.18	116.36	77.95	253.68	212.31	107.98	90.83

[a]Different lower-case letters in the same column indicate a significant difference ($p < 0.05$) between different k values.

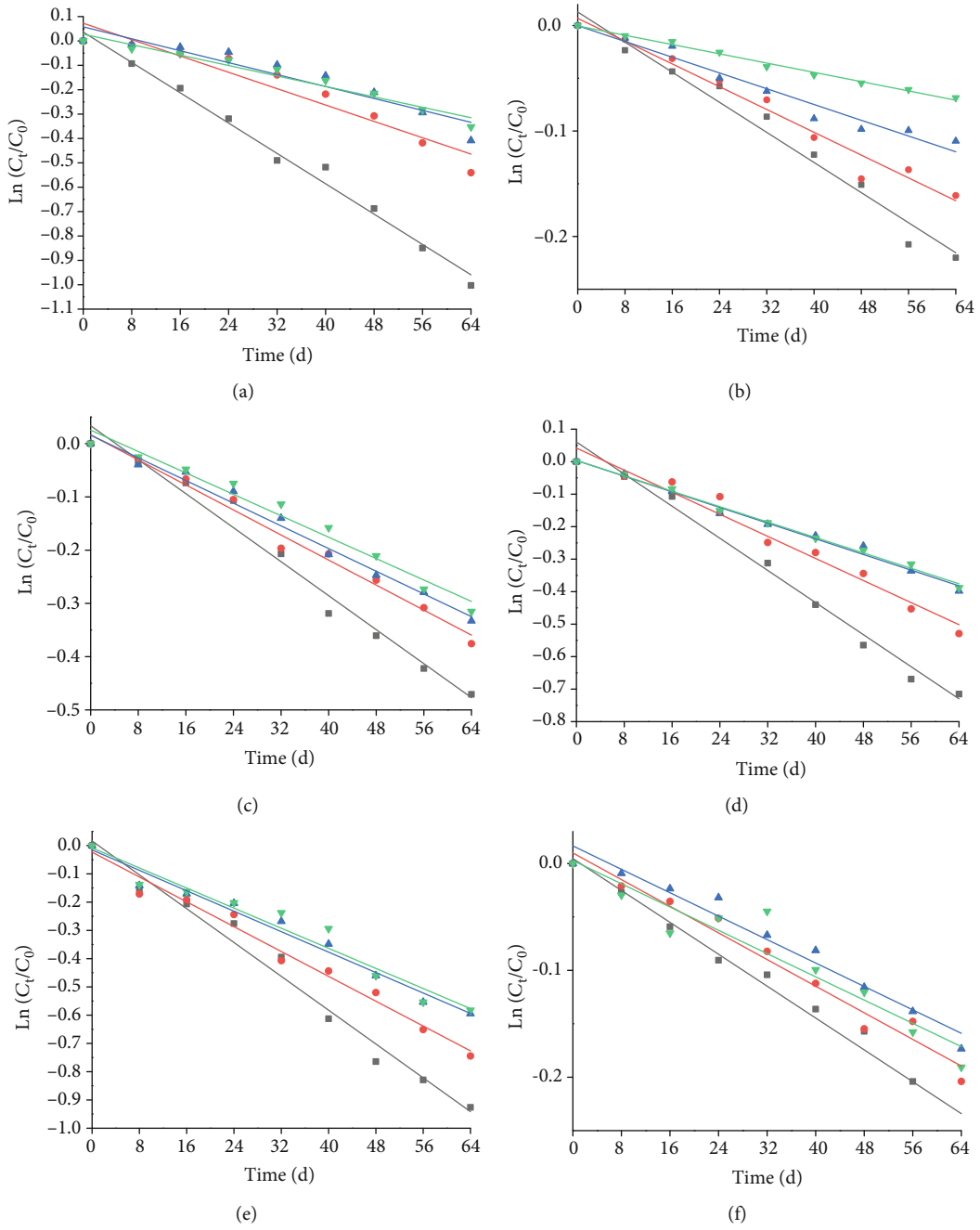

Figure 6: Continued.

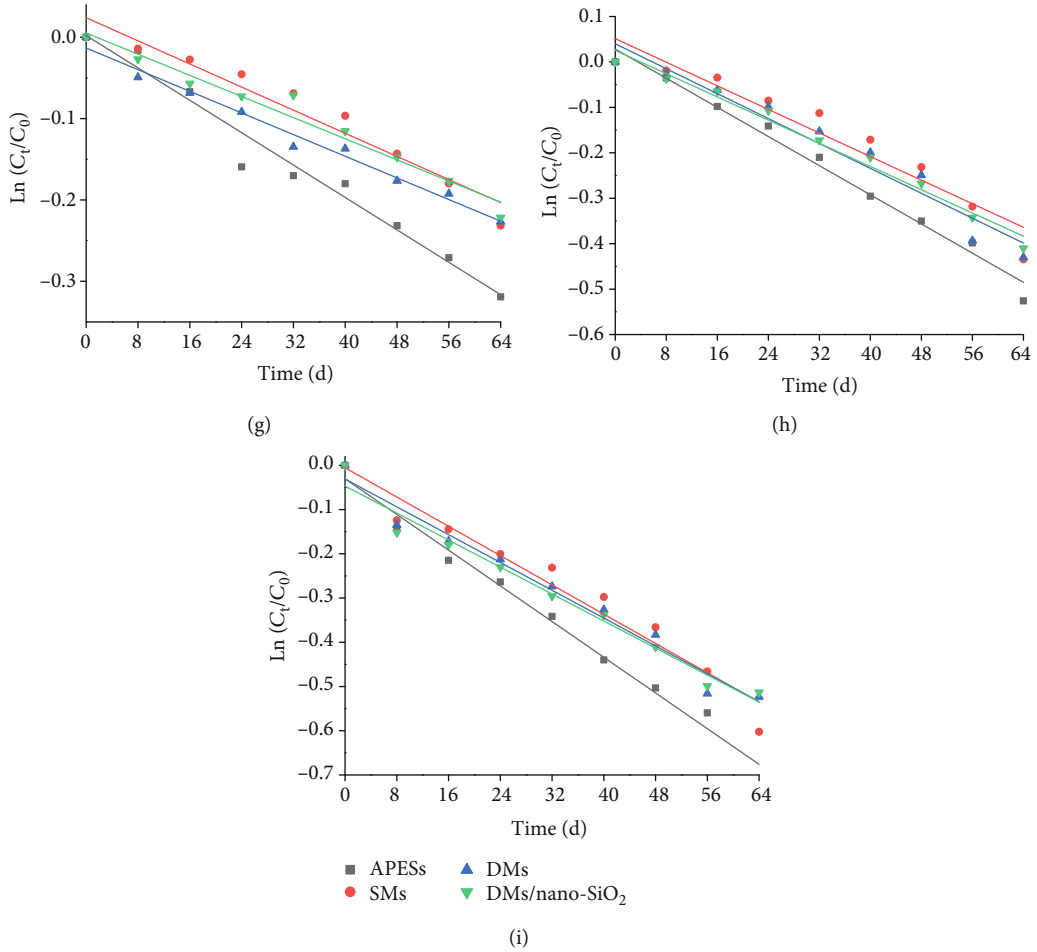

Figure 6: The first-order kinetic plots for APESs, SMs, DMs, and DMs/nano-SiO_2 during different storage conditions. (a) The first-order kinetic plots for samples under light. (b–e) The first-order kinetic plots for samples under different temperatures (4, 20, 40, and 60°C). (f–i) The first-order kinetic plots for samples under different relative humidities (11, 33, 53, and 75%).

As shown in Table 1 and Figures 6(f)–6(i), the storage stabilities of anthocyanins were influenced by the relative humidity. At 11% of the relative humidity, the $t_{1/2}$ values of APESs, SMs, DMs, and DMs/nano-SiO_2 were 188.49, 221.15, 251.82, and 253.68 d, respectively. The $t_{1/2}$ value of SMs, DMs, and DMs/nano-SiO_2 increased by 17.33%, 33.60%, and 34.59%, respectively, compared with APESs. The results indicated that the addition of nano-SiO_2 had a positive protective effect on the preservation of anthocyanin microcapsules. In recent years, many studies have shown that nano-SiO_2 can improve the water resistance and mechanical properties of the composite films containing nano-SiO_2 [21, 35, 43, 45]. The $t_{1/2}$ value of DMs/nano-SiO_2 is 253.68, 212.31, 107.98, and 90.83 d at 11%, 33%, 53%, and 75% of the relative humidity, respectively. These results were attributed to the changes in swelling, permeability, and mechanical strength of wall materials caused by high humidity, which resulted in the core material to flow out or react with other external materials. The high-humidity environment increased the moisture content and damaged microcapsules.

4. Conclusions

In this paper, the characteristics of SMs, DMs, and DMs/nano-SiO_2 of APESs were studied. The results were as follows:

(i) The double-embedding technology can improve EE, thermal stability, and storage stability compared with the single-layer microencapsulation technology especially when nano-SiO_2 is added to the wall material of the microencapsulated anthocyanin of APESs. The EE of DMs/nano-SiO_2 was 97.85%, and the moisture content was 2.17%. SEM images showed that the surface of the microcapsules was smooth. The t_m of DMs/nano-SiO_2 was 156.12°C, and it was 73.61°C and 45.33°C higher than those of SMs and DMs, respectively

(ii) The addition of nano-SiO_2 enhanced the storage stability of microcapsules, and it could keep longer $t_{1/2}$ under high temperature and relative humidity

(iii) Double-layered microcapsules containing nano-SiO_2 can promote the storage stability of the microencapsulated anthocyanin of APESs. This technology has broad prospects in the application of microcapsule technology

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Xue Sun and Jingcheng Su *contributed equally to this study.*

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