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Geranium Wilfordii Maxim이 봉입된 마이크로캡슐의 제조와 체외방출 성능

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Preparation and *In-Vitro* Release Performance of Geranium Wilfordii Maxim Filled Biodegradable Microcapsules

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Abstract: Encapsulation of Geranium wilfordii Maxim (GWM) into polyvinyl alcohol (PVA) biodegradable microcapsules was performed using the interfacial polymerization method. The optimum synthesis conditions including the core/shell ratio and the emulsifier concentration were explored. The fabricated microcapsules were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The *in-vitro* release behaviour of the GWM microcapsules was studied by ultraviolet-visible spectroscopy (UV-VIS). The results show that when the core/shell ratio was 1:1 and the emulsifier concentration was 5%, the GWM microcapsules sizes have a normal distribution with a mean diameter of 23.94 μm. FTIR results show that the GWM was successfully encapsulated by the PVA polymer. TG results indicate that the GWM microcapsules are stable below 300 °C. Moreover, the release from the GWM microcapsules occurs according to a non-Fickian diffusion model.

Keywords: traditional Chinese medicine extractive, microcapsule, slow-release, interfacial polymerization.

Introduction

Traditional Chinese medicines (TCM) have a longstanding history in the clinical treatment of diseases because of their good pharmacological activity and low toxicity.[1] The water extracts of Geranium wilfordii Maxim (GWM) have demonstrated anti-inflammation and anti-oxidation properties,[2,3] which can be used for treating rheumatism and arthritis.[4,5] The conventional way is to make GWM into plaster or paste and attach it to the skin of the patients,[6] so that the active ingredients can be delivered to the skin of the affected area through transdermal absorption. This therapy is very effective, but there are considerable side effects. For example, the matrix of traditional plaster contains a certain amount of lead tetroxide, which may lead to saturnism during the treating process.[7] In order to solve this problem, researchers replaced the lead tetroxide matrix with the nontoxic hydrophilic and invented the cataplasm.[8-10] However, the cataplasm also has to be pasted on skin, which makes the patient discomfort. In addition, it is easy to come off when the cataplasm posted on the joints. As a result, it is necessary to develop new methods to reduce the discomfort degree of patients, for example, drug-loaded tights and wearable supports. These drug-loaded textiles can keep drugs contact with skin without any adhesives because of their excellent elasticity. At the same time, the air permeability of the textiles will decrease the discomfort degree.[11] For drug-loaded tights and wearable supports, the textiles should have not only slow-release property and thermal, chemical stability but also elasticity and air permeability. The drug-loaded textiles can be made in various techniques such as printing, padding, immersion, coating,[12] UV and microwave irradiation. Using these techniques, textiles would be compounded with other materials successfully at a high temperature, therefore, the chemical and thermal stability of

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drugs loaded on the textiles become very important.[13] Most of the drugs are sensitive to chemical environment when mixed with other materials, and are released at a short time which cannot fully take effect for users. Therefore, a suitable carrier can give drugs slow-release property and improve their chemical and thermal stability.

Microencapsulation has been investigated to be an effective way to give drugs slow-release property. Using this technology, soluble or insoluble drugs can be coated by polymer shells[13] and protected from being affected by environment conditions.[14] It is very suitable for drug delivering system. Compared with oral taking and bolus injection, the microcapsules will bring drugs a relatively longer onset time and avoid drugs degradation caused by first-pass hepatic metabolism.[15] Many kinds of natural and synthetic polymers, which can form semipermeable membranes under specific conditions, are used to form microcapsule shells including Calcium-alginate,[16] chitosan,[17,18] poly(allylamine hydrochloride),[19] polyvinyl alcohol (PVA),[20-22] polymethyl methacrylate (PMMA)[23] and poly-*L*-lysine.[24] Depending on the physical and chemical properties of both the encapsulated substance and the capsule materials, researchers can apply a microencapsulation method, ranging from the internal phase separation,[25] the multiple emulsion method,[26] and *in-situ* polymerization[27,28] to interfacial polymerization,[20] double emulsion-solvent evaporation,[29] layer-by-layer polyelectrolyte self-assembly,[30] and complex coacervation.[31] Most of the researchers focused on the microencapsulation of insoluble drugs for *in-vivo* release use,[18-21,24,30-33] but the microencapsulation of soluble drugs for external use is rarely studied.

This study focused on the microencapsulation of soluble water extract of GWM through interfacial polymerization method. The wall material was prepared by a condensation reaction of PVA and glutaraldehyde (GA) in acid medium. PVA is used as the wall material of the microcapsules due to its innocuous, non-carcinogenic, biodegradable and biocompatible properties.[34] Compared with other polymerization methods as abovementioned, the interfacial polymerization method was simpler, more cost-effective, and more efficient.[35] Through interfacial polymerization, PVA microcapsules filled with the water extracts of GWM were manufactured, and the release control properties could have potential applications in wearable supports and tights. To achieve this goal, SEM, FTIR, TG, and UV-VIS techniques were used to determine optimal preparation conditions, particle sizes, swelling and release properties.

Experimental

Reagents. Water extracts of GWM (10:1, powder) was purchased from Xi'an Runxue Biotechnology Co. Ltd (China). Polyvinyl alcohol (PVA, (Mw) = 1788±50) was obtained from Chengdu Kelong Chemical Co. Ltd (China). *N*-hexane was supplied by Tianjin Zhiyuan Chemical Co. Ltd (China). Span-80 (HLB = 4.3) was purchased from Shanghai Shenyu Pharmaceutical & Chemical Co. Ltd (China). Hydrochloric acid (36 wt% water solution) and sodium hydroxide were supplied by Tianjin Fengchuan Chemical Reagent Technologies Co Ltd (China). Glutaraldehyde (25 wt% water solution) and phosphate buffer saline (PBS, pH = 6.68) were obtained from Tianjin Damao Chemical Reagent Factory (China).

Preparation of PVA/GWM Microcapsules. PVA was used as the capsule wall materials and the extracts of GWM were used as the encapsulated core materials. During the preparation processes PVA (4 wt% water solution) and GWM extracts (5 wt% water solution) were mixed in varying weight ratios (3:2, 1:1, 2:3, and 1:2) at a speed of 3000 rpm by a homogenizer (XHF-D, Scientz, China). Then, 6 g of the mixture was added to 40 mL *n*-hexane containing a 5% mass fraction of the surfactant span-80, heated to 30 °C in a water bath, and agitated using a mechanical stirrer (DW-3-50, Yuhua Instruments, China) at a speed of 500 rpm for 20 min. After that, the cross-linking agent and catalyst, a mixture of 2.0 mL GA and 0.1 mL hydrochloric acid, were added dropwise to the system at the speed of 0.4 mL/min. Then the mixture was kept stirring for another 60 min at the speed of 500 rpm. Afterwards, the pH of the reaction system was adjusted to 6~7 using 5 wt% sodium hydroxide solution. The microcapsule slurry was decanted on filter paper twice and rinsed with distilled water. The rinsed microcapsules were dried at room temperature (25 °C) for 24 h to remove water on the microcapsules' surfaces. The microcapsules were obtained by extraction filtration and were rinsed with isopropyl alcohol and distilled water. After that, they were dried in air.

Imaging and Particle Size Analysis of the PVA/GWM Microcapsules. The structure of the PVA/GWM microcapsules was investigated using a scanning electron microscope (SEM, S4800, Hitachi, Japan). The sample was covered with a layer of gold in vacuum conditions. The particle size of the microcapsules was determined from the SEM images using the NanoMeasurer® software. More than 300 microcapsules were investigated to obtain statistically significant results. The monodispersity coefficient was calculated using eq. (1) and (2).[36]

$$\delta = \left[\frac{\sum_{i=1}^{n} (D_i - \overline{D})^2}{n-1} \right]^{\frac{1}{2}} \quad (1)$$

$$\varepsilon = \frac{\delta}{\overline{D}} \quad (2)$$

Where D_i is the diameter of one microcapsule, $\overline{D}$ is the mean diameter of microcapsules, and n represents the total number of microcapsules. The δ denotes the standard deviation of the microcapsules, and ε represents the dispersion coefficient.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis. FTIR spectral data of the GWM extracts, microcapsules, and the wall materials were obtained using an FTIR spectrophotometer (TENSOR37 FTIR, Bruker Corporation, Germany) to confirm the formation of the copolymer. The specimens were prepared by compressing KBr pellets. The samples were investigated in a spectral window ranging from 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1}.

Thermogravimetric Analysis. The thermal stability was measured by a thermogravimetric analyzer (TG, STA 449F3, Netzsch, Germany), at a scanning rate of 10 ºC·min^{-1} between the temperature of 40~630 ºC in a nitrogen atmosphere.

Release Properties of the PVA/GWM Microcapsules. In a preliminary study, the maximum absorbance wavelength of GWM solution was found to be 310.5 nm by a UV-VIS spectrophotometer (UV2401PC, Shimadzu, Japan). The correlation of the GWM concentration (x) and absorbance intensity (y) was expressed in eq. (3) using a UV-VIS spectrophotometer at 310.5 nm. It showed that x and y were in a good linear correlation because of $R^2 = 0.99925$.[37] Because the P value was 5.71002×10^{-6}, which is much smaller than 0.05, the GWM concentration (x) and absorbance intensity (y) could be considered as having a positive correlation according to analysis of variance.

$$y = 2.36x + 0.03 \quad (R^2 = 0.99925) \quad (3)$$

In order to obtain the release data of the GWM extracts from the microcapsules, 10 mg of PVA/GWM microcapsules were dispersed into 30 mL phosphate buffer solution (PBS, pH = 6.68) and incubated at 30 ºC in a water bath, stirring at 100 rpm. Aliquots (3 mL) were withdrawn at 1 h intervals and the dissolution media was replenished with fresh PBS to maintain the total volume after each withdrawal.[37,38] Data was collected by a UV-VIS spectrophotometry at the maximum absorbance wavelength of 310.5 nm.

To determine the release profile of the GWM extracts, the relationship between the drug concentration and time was plotted in a diagram. The release curve was calculated from the ratio between the concentration of the drug at specific time and at equilibrium using several different release models including Zero-order, First-order, Higuchi and Ritger-peppas models.[39,40]

Swelling Property of the PVA/GWM Microcapsules. In the swelling experiment, 10 mg of PVA/GWM microcapsules were first dispersed into 30 mL PBS solution (pH=6.68), and then incubated at 30 ºC in a water bath and stirred at 100 rpm. The microcapsules were weighted at per 1 h after being centrifuged and blotted with filter paper to remove surface water.

The swelling degree S_t and equilibrium swelling degree S_e were calculated by eq. (4) and (5).[41]

$$S_t = \frac{W_t - W_d}{W_d} \quad (4)$$

$$S_e = \frac{W_e - W_d}{W_d} \quad (5)$$

Where W_d is the initial weight of the dry microcapsules, W_t is the weight at any time t. W_e represents the equilibrium weight during the water absorption.

Results and Discussion

Influence of Emulsifier Concentration on Morphology. The emulsifier concentration was greatly dependent on the interfacial tensions between the immiscible two-phase systems. The interfacial tension determined the dispersion state of the dispersed phase droplets and finally determined the morphology of the microcapsules. Very high interfacial tension made the emulsions unstable, while very low interfacial tension made it difficult for the dispersed phase droplets to maintain spherical in the emulsions.[29] To study the effects of emulsifier concentration, six emulsifier concentrations were selected (0, 1, 3, 5, 7, and 9 wt%), other parameters were fixed as follows: 1:1 core/shell weight ratio, 40 mL *n*-hexane, 2.0 mL GA, 0.1 mL hydrochloric acid, 500 rpm agitator speed, reaction temperature 30 ºC, and reaction time 90 min. Figure 1 shows the effect of emulsifier concentration on the morphology of PVA/GAM microcapsules.

Figure 1(a) and 1(c) indicate that low emulsifier concentration could not effectively reduce the interfacial tension

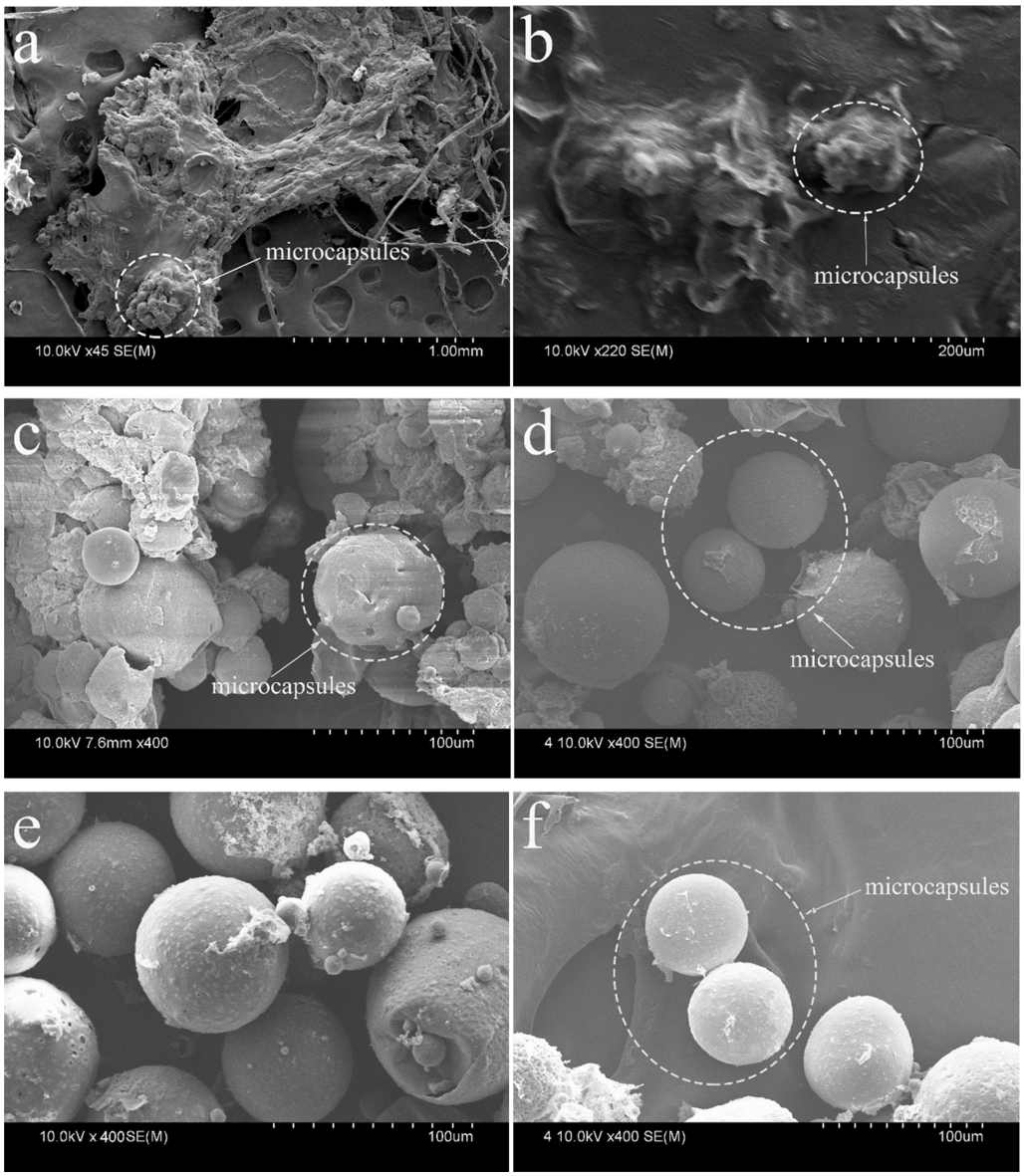

Figure 1. SEM images of PVA/GWM microcapsules prepared with different emulsifier concentrations: (a) 0%; (b) 1%; (c) 3%; (d) 5%; (e) 7%; (f) 9%.

between the PVA/GWM extract composite and *n*-hexane, resulting in the unevenly dispersion of the PVA/GWM extract composite in *n*-hexane at a relatively low stirring speed of 500 rpm. As a result, the unevenly dispersed liquids cross-linked with each other and formed a thick, fiber-like solid. As seen in Figure 1(a), the conglutination between microcapsules was much more pronounced when prepared without emulsifier. The appropriate emulsifier concentration (Figure 1(e) and 1(f)) allowed for the dispersion of the droplets in *n*-hexane, while relatively low interfacial tension prevented the droplets from excessive contacting and adhering. However, when the emulsifier concentration was used in excess (Figure 1(f)), the composite droplets and GA droplets could hardly contact with each other and react at the interface. Thus, few composite droplets could be converted to microcapsules. The differences between Figure 1(e) and 1(f) indicate that a 5 wt% emulsifier concentration was suitable for the preparation of the microcapsules.

Influence of Core/Shell Weight Ratio on Surface Morphology. In order to study the effect of core/shell weight ratios, five weight ratios were chosen (2:1, 3:2, 1:1, 2:3, and 1:2). The emulsifier concentration was fixed at 5 wt%, and all

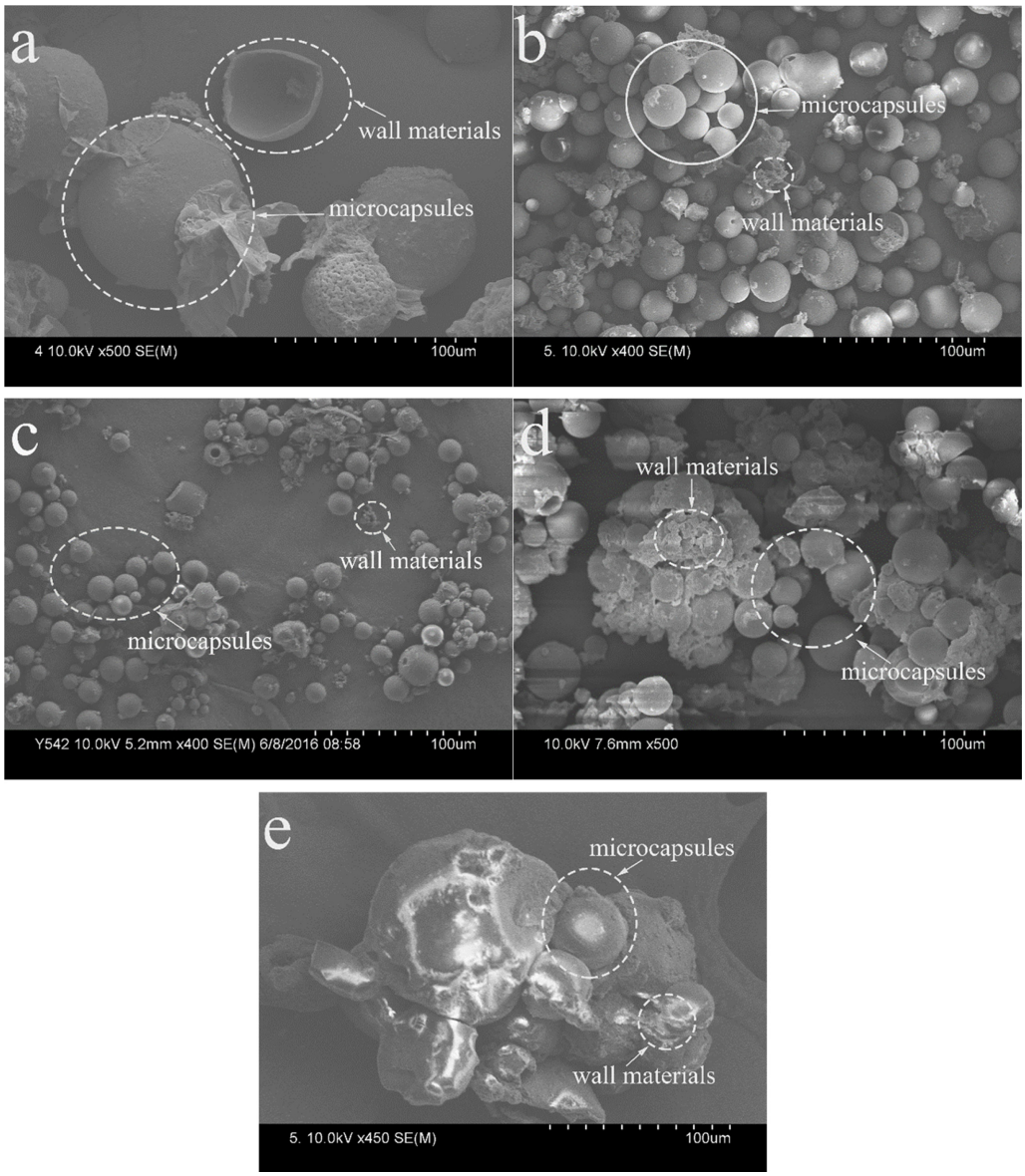

Figure 2. SEM images of PVA/GWM microcapsules prepared with different core/shell weight ratios: (a) 2:1; (b) 3:2; (c) 1:1; (d) 2:3; (e) 1:2.

other parameters were kept the same as described in the previous section. Figure 2 shows the effect of various core/shell weight ratios on surface morphology. According to Figure 2(a) and 2(b), the microcapsules have a relatively smooth outer surface and show little adhesion. However, the UV-VIS spectrum of the raffinate shows that there are large amounts of non-encapsulated core materials after the synthesis. Lack of wall materials makes it difficult to encapsulate most of the core molecules into the microcapsules, wasting large amounts of the core materials. Figure 2(d) and 2(e) show that when the core/shell weight ratio was low enough, the excess shell materials cross-linked with the microcapsule shells, leading to the formation of irregular lumps during the synthesis. The adhesion was much more pronounced when the core/shell weight ratio decreased and the lumps became larger. Microcapsules shown in Figure 2(c) have smooth surfaces and show no adhesion. It can be concluded that the core/shell weight ratio of 1:1 is optimal for the preparation of the PVA/GWM microcapsules.

Structure and Particle Size Distribution. Figure 3(a) shows the outer surfaces of the PVA/GWM microcapsules prepared under optimized conditions. All the microcapsules show relatively smooth outer surfaces and few microcapsules are broken during the preparation process. Figure 3(b) indicates that the outer surfaces of the microcapsules are very compact,

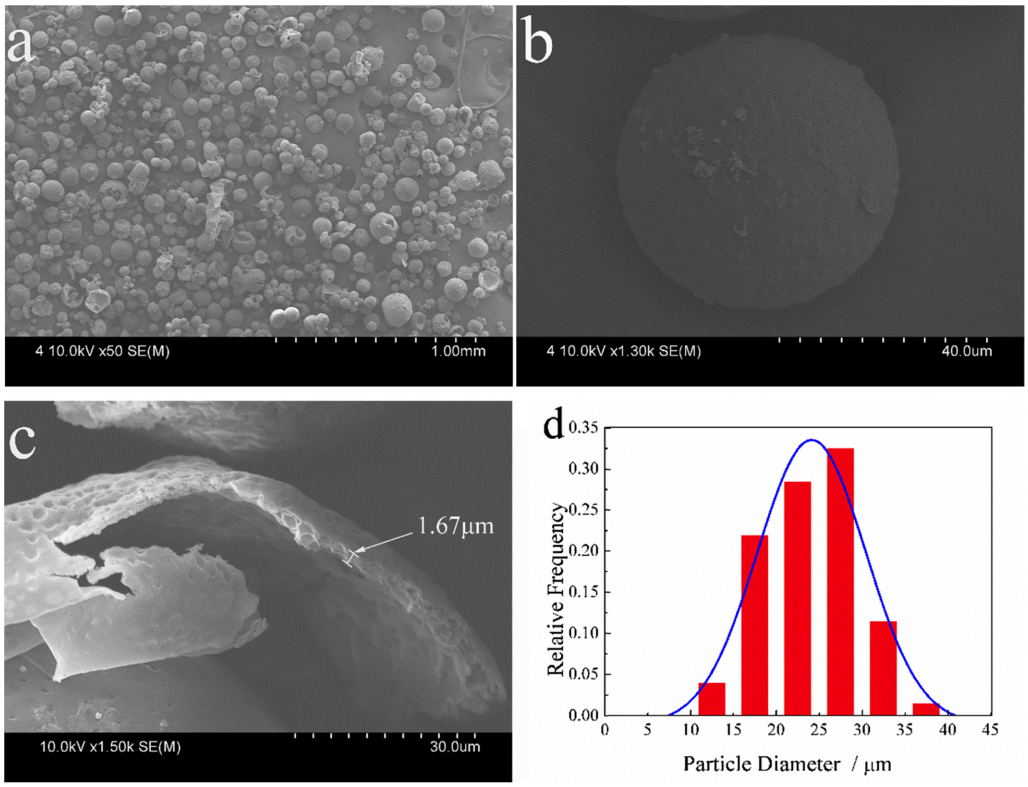

Figure 3. SEM images of (a) microcapsules prepared under optimized synthesis conditions; (b) outer surface of a single microcapsule; (c) the core-shell structure of the microcapsule; the graph of (d) particle size distribution of PVA/GWM microcapsules.

effectively preventing the break of the microcapsules during the synthesis. Figure 3(c) shows the core-shell structures of the PVA/GWM microcapsules. The thickness of the shell is about 1.67 μm. Quantitative measurement of the size distribution was conducted using NanoMeasurer® software and shown in Figure 3(d). The size distribution graph indicates that the particle sizes of the PVA/GWM microcapsules are almost identical and have a mean diameter of 23.937 μm. The dispersion coefficient ε calculated according to eq. (1) and (2) is 0.07, which means that the particle sizes are relatively uniform. This particle size is appropriate to prolong the release time of the drug. In addition, it shows no adverse effects on coated textiles.

FTIR Spectra of PVA/GWM Microcapsules. Figure 4(a) displays that peaks at 1167.46 and 1027.53 cm^{-1} (C-O stretching vibration), and 767.14 cm^{-1} (-OH bending vibration) indicated the existence of phenolic compounds. The wider peak of -OH stretching vibration at 3292.67 cm^{-1} can also improve the existence of phenolic compounds. The FTIR spectrum of the shell is shown in Figure 4(c). The peak at 2928 cm^{-1} refers to the C-H stretching vibration from alkyl groups. The peak at 1732.96 cm^{-1} due to the C=O and C-O stretching vibration

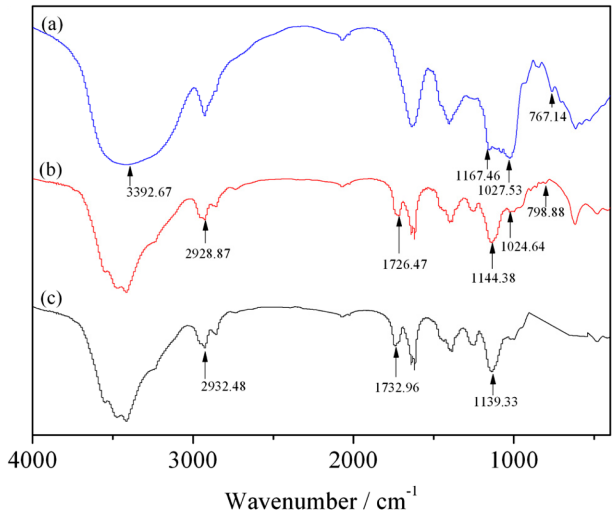

Figure 4. FTIR spectra of the GWM extracts (a); PVA/GWM microcapsules (b); the shell (c).

from acetate group remained in the PVA.[42] The C-O stretching vibration at 1139.33 cm^{-1} relates to the formation of C-O-C group and shows the PVA has been crosslinked with GA.[20] Characteristic peaks of GWM at 1144.38, 1024.64, 798.88 cm^{-1},

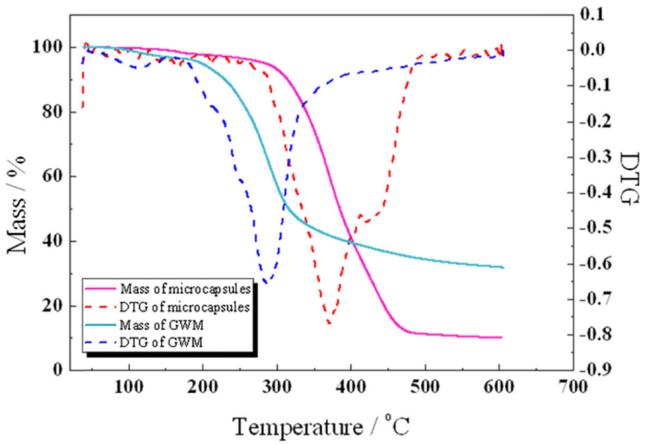

Figure 5. TG and DTG curves of GWM and microcapsules.

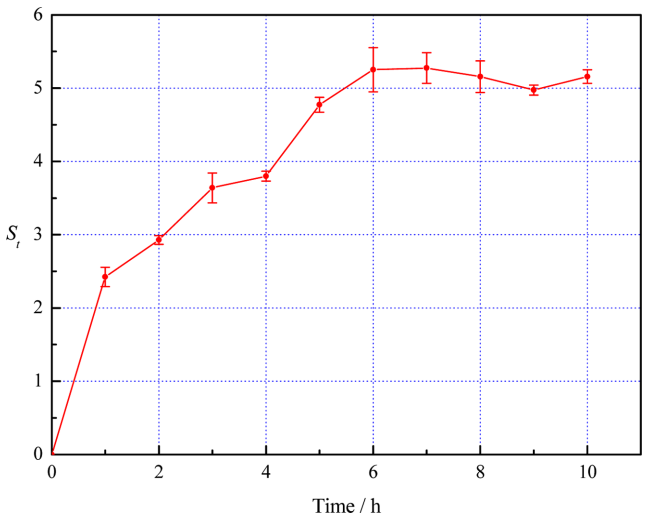

Figure 6. Swelling curve for the PVA/GWM microcapsules.

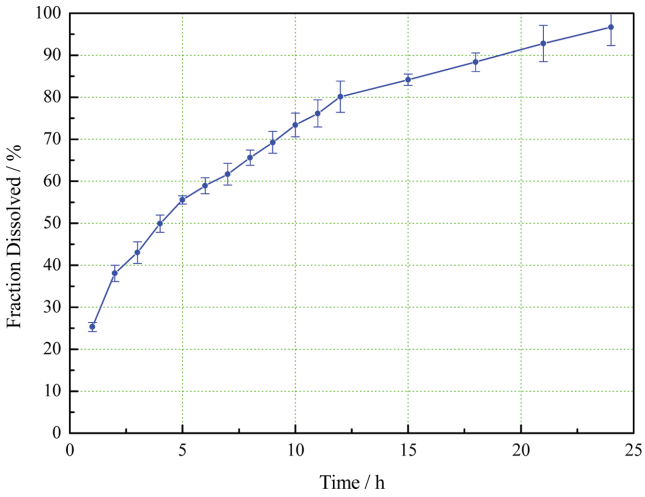

Figure 7. Release curve of PVA/GWM microcapsules.

and that of the shell at 2928.87, 1726.96 cm^{-1} could be found in the spectrum of the PVA/GWM microcapsules (Figure 4(b)), which shows that the GWM has been encapsulated successfully.[43]

Thermal Stability of PVA/GWM Microcapsules. TG was used to evaluate the thermal stability of the core materials and the PVA/GWM microcapsules. The results of TG experiments (Figure 5) reveal that the water extracted powder of GWM start losing weight at about 82 ºC, and substantial weight loss occurrs when it was heated to 246 ºC. The residual mass may be attributed to impurities. The PVA/GWM microcapsules show an excellent thermal stability when they were heated up to about 300 ºC, and substantial weight loss appeared only at 325 ºC. This result suggests that the shell will be able to protect the core materials in curing processes which expose textiles to 120~180 ºC.[44,45]

Swelling and *In-vitro* Release Properties. According to eq. (5), the equilibrium swelling degree S_e of the PVA/GWM microcapsules is 5.276. The swelling curve (Figure 6) shows that the PVA/GWM microcapsules can absorb water and keep on swelling until reaching the equilibrium swelling degree. This process lasts for about 6 h. Compared with the other time periods, the PVA/GWM microcapsules absorbed the most water during the first hour. A large quantity of absorbed water makes the microcapsules swelling fast. On the same time, drugs absorbed in the superficial layer of the microcapsules may be diffused into PBS and finally lead to a burst release.

The release curve (Figure 7) shows that the PVA/GWM microcapsules had excellent *in-vitro* release properties. The drug release process could be divided into three steps: the burst release step (0~1 h), the fast diffusion step (1~20 h) and the slow diffusion step (20~24 h).[43] During the first step, the dissolution of drugs which are absorbed to the superficial of the microcapsules leads to minor burst effects. This finding corresponds to that of swelling test in the first 1 h. In the second step, the swelling of the shell induced by the high osmotic pressure causes the drug molecules to release in the core area at a relatively high rate. During the last step, the drug in the core area is almost completely diffused out. Consequently, the release is slowed down due to the low osmotic pressure. This release behavior was similar to that reported by Bian.[46] In order to understand the release mechanism of the PVA/GWM microcapsules, release curves were calculated using different release models. The outcome of the curve fittings is shown in Figure

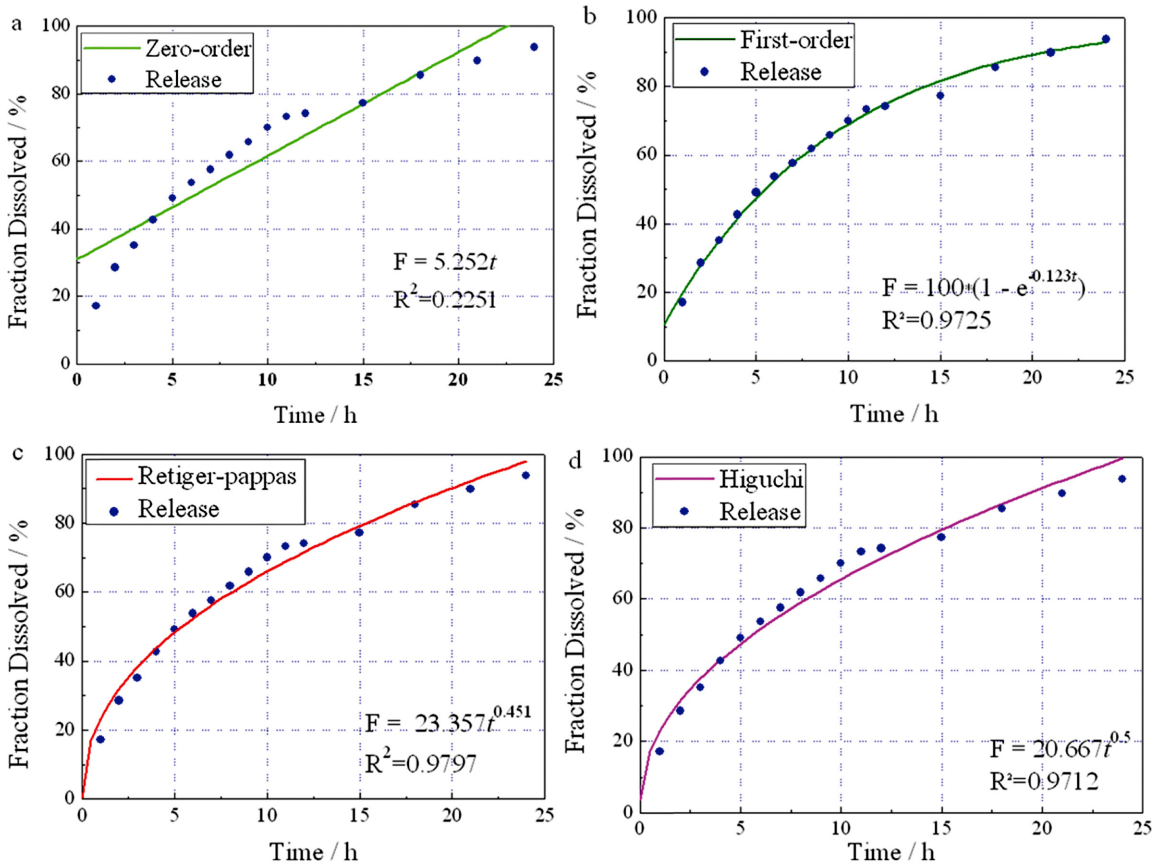

Figure 8. Fitting curves for the zero-order model (a); first-order model (b); Retiger-Pappes model (c); Higuchi model (d).

Table 1. Assessment of the Drug Release Mechanism according to the Ritger-Peppas Model

Release exponent (n)	Drug release mechanism
$n \leq 0.45$	Fickian diffusion
$0.45 \leq n \leq 0.89$	Non-Fickian diffusion
$n \geq 0.89$	Bull erosive release

8. The result indicated that the observed release pattern fits better with the Ritger-Peppas model ($R^2 = 0.9797$), implying that the release mechanism is associated with non-Fickian diffusion. Because the non-linear fitting gives k values within the range of $0.45 < k < 0.89$ (Ritger-Peppas model), the mechanism can be classified as non-Fickian diffusion (Table 1).

When the PVA/GWM microcapsules are used for tights and wearable supports, the microcapsules would not be entirely wetted in a short time. Therefore, they would be hardly able to swell completely and diffuse out in a short time. For simulate the use environment of the microcapsules, microcapsules are tested at 30±5 ºC and 50±10% RH for about 3 months. After 3 months, 60.42% of GWM are still remained in the microcapsules, which shows a slow release for the microcapsules.

Conclusions

PVA/GWM microcapsules with a 23.94 μm mean diameter were successfully prepared through interfacial polymerization. The microcapsules have relatively smooth outer surfaces with little adhesion. FTIR experiments showed that the GWM extracts had been confined in the microcapsules. TG tests indicated that the thermal stability of the GWM extracts was significantly improved through the process of microencapsulation. The *in-vitro* release studies showed that the drug is released over a time frame of more than 24 h. Its release mechanism can be classified as non-Fickian diffusion, a combination of Fickian diffusion and matrix erosion. The simulation use environment test proves that the microcapsules show a slow-release in a long term. In conclusion, these controlled-release PVA/GWM microcapsules can be applied as drug-loaded wearable supports and tights in the future.

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