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Preparation and Properties of Olive Oil Microcapsules

Danfeng Yu, Wenjing Qiao, Qiuyu Li, Guangling Pei*

School of Materials Science and Engineering, Beijing Institute of Fashion Technology
Beijing 100029, China

Abstract

In this paper, microcapsules were produced by complex coacervation using gelatin and acacia as wall materials and olive oil as the core substance. Process parameters, such as the dosage of the crosslinker, concentration of the wall materials, pH Value and the ratio between core and wall materials were analyzed in detail. Moreover, crosslinking degree of wall materials was more important in obtaining good slow release microcapsules. The morphology and particle size distribution of the microcapsules were analyzed by scanning electron microscope and laser particle size analyzer. The oil content and the release rate of the olive oil were also studied. In order to obtain microcapsules with good mobility and dispersal, a spray drying process was used to dry the product. The olive oil microcapsules were obtained with particle size of 3∼8 μm, and an oil content of about 60%. The optimum process parameters were as follows:dosage of the cross linking agent was 3 ml, the concentration of wall materials was 3%, the pH value of coacervation was 4.0 and the ratio of core/wall material was 1:1. Olive oil microcapsules prepared with these optimal process conditions had good disperse effect and high encapsulation efficiency.

Keywords: Gelatin; Microcapsules; Complex Coacervation; Olive Oil; Arabic Gum

1 Introduction

Microencapsulation has been widely used in applications such as the controllable release of drugs and improvement of the stability of core substance and many other fields. Volatile liquids and solids are easily damaged during long-term use, due to their external environment, and this leads to the degradation of mechanical properties and even loss of function. It is possible to prevent this by embedding them into polymer wall materials, forming microcapsules [1]. Complex coacervation is an important method which is widely used to prepare microcapsules for controllable drug release because of its simplicity and low pollution. In this method, two or more than two kinds of molecules of opposite charge are joined as the walls, and then disperse the core substance into the aqueous solution of wall materials. When the conditions are right, the wall materials will attract with each other because of the opposite charges, and then embed the core material [2]. Research of complex coacervation technology is very helpful in order to increase the yield and quality of microcapsules and actual production process [3]. Spray drying is a commercial process

*Corresponding author.
Email address: clypgl@bift.edu.cn (Guangling Pei).

which is widely used in large-scale production of encapsulated flavors and volatile. The merits of process have ensured its dominance; these include availability of equipment, low process cost, wide choice of carrier solids, good retention of volatiles, good stability of finished product, and large-scale production in continuous mode [4]. In recent years, the technology of microcapsules has played an important role in preparing functional textile [5].

The gelatin–arabic gum couple has been known for a long time to undergo complex coacervation and serve well as a wall-forming material for microcapsules [6]. The primary reasons to use gelatin and arabic gum as wall materials are their abundance and biodegradability. The fact that the charge on gelatin is pH-dependent makes this method of preparation of microcapsules extremely dependant on pH and hence it is easy to control the reaction [7].

Olive oil is a natural green vegetable oil which is abundant in vitamin, carotene and many trace elements and it has many functions in nutrition and health care [8]. Olive oil is rich in the essential fatty acidsVitamin A, D, E, K and other antioxidant substances which can be rapidly absorbed by the body and can maintain skin elasticity and moisture. These substances can be absorbed through the skin and make it glossy and soft, as well as promoting blood circulation and skin metabolism. It can also help to lose weight, reduce wrinkles, and slow down signs of aging. The unsaturated fatty acids are able to fight cancer, and phenols can help to reduce radiation [9].

In this paper, gelatin and arabic gum are used as wall materials to obtain microcapsules that can be controlled to release the core substance. Complex coacervation was used to first carry encapsulation and spray drying was later used to dry the microcapsules. The first layer of microcapsule was received by complex coacervation and the second layer of microcapsule was obtained by following spray drying. Microcapsules prepared by this method can resist higher temperature.

2 Experiment

2.1 Materials

The Arabic gum was purchased from Tianjin Guangfu Fine Chemical Research Institute (Analytically Pure). The gelatin was purchased from Chemical Reagent Factory of Tianjin Fu Chen (Biochemistry Reagents). Olive oil was purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd (Chemical Pure). Citric Acid (20%) and saturated sodium carbonate were prepared in lab to adjust pH.

2.2 Preparation of Microcapsules

The olive oil microcapsules were prepared by complex coacervation and spray drying. Firstly, arabic of 1.5 g was dissolved in 50 ml water and was added into four-neck flask with agitation, thermometer and condensator. The stirring rate and temperature of reaction system were adjusted to 1000 rpm and 45℃ respectively. Then olive oil of 3 g was poured into after the Arabic gum fully dissolved. Lastlythe gelatin solution with the concentration of 3% was added into four-neck flask. The pH of system was adjusted to 4.0 with citric acid (20%) after 30 minutes. The coacervation reaction started and reaction was kept for some time. Stop the heating and remove off the hot water when the reaction was up 2 hours and cool down the solution in air. When the temperature became around 30℃-35℃, some ice blocks was use to lower the temperature below

10℃. Then glutaraldehyde solution was used to crosslink the wall materials and the pH of system were adjusted to 9.0 in 30 minutes. The reaction was kept for 2 hours before it was over. To get powdered microcapsules, the solution was fed to the spray dryer. The inlet temperature was 180℃ and outlet temperature was 90℃. The microcapsules were collected for further analysis.

2.3 Analysis and Detection

2.3.1 Drug-loading Rate

Drug-loading rate of microcapsules was determined by solvent extraction using methylene dichloride as the extracting agent and the extraction process lasted for 4 hours. The drug-loading rate was calculated using follow formula:

$$\text{drug-loading rate}(\%) = (\text{m} \,/\, \text{M}) \times 100\%$$

Here, m represents the quality of microencapsulated olive oil, M represents the quality of microcapsules used in the extraction.

2.3.2 Particle Size and Particle Size Distribution

The particle size and particle size distribution were determined by a laser particle size analyzer (Malvern Instruments Ltd, United Kindom).

2.3.3 Morphology of the Microcapsules

The morphology of the microcapsules was observed with scanning electron microscope (JEOL, Japan).

2.3.4 Thermal Decomposition and Release Rate

A vacuum oven was used to determine the release rate of the microcapsules and the TGA (PRT-1) was used to analyze the decomposition temperature.

3 Results and Discussion

3.1 IEP of Gelatin

Gelatin (GE) is a biodegradable polypeptide polyampholyte derived from denatured collagen lacking any secondary and tertiary structure. When pH values are below the IEP, the gelatin is positively charged because of the protonation of amino groups. Whereas when pH values above the IEP, it is negatively charged due to the ionization of carboxyl groups, and repels the like-charged counterpart [10]. The Isoelectric Point (IEP) of the gelatin used in the experiment was tested as follow.

Firstly, 40 ml gelatin solution (3%) was prepared and was kept at 45 ℃. Then 0.2 ml standard solution of sodium hydroxide (1%) was added into the gelatin solution. A conductivity analyzer was used to determine the electrical conductivity (EC) and a pH meter was used to determine the corresponding pH. The electrical conductivity and pH of solution were analyzed every time after 0.2 ml standard solution of sodium hydroxide was added. The result is shown in Fig. 1. From the figure, it can be seen that the IEP of gelatin is 9.22. It is illustrated at the lower point of the curve. Here the positive charges equal the negative charges.

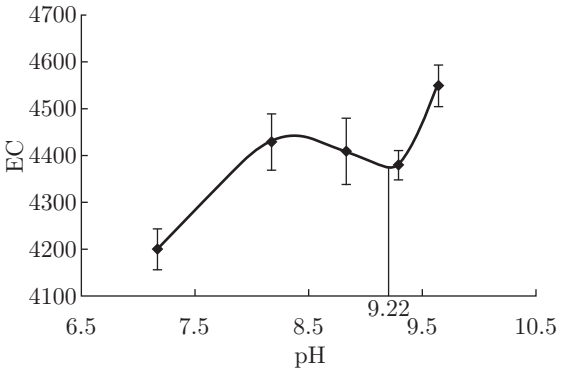


Fig. 1: Relationship between the conductivity (κ) and pH value of gelatin solutions

3.2 Influence of Amount of Cross Linking Agent

Glutaraldehyde solution was used as the cross linking agent. The amount of glutaraldehyde influenced the particle size and drug-loading rate of microcapsules. Results tested are shown in Fig. 2 and Table 1.

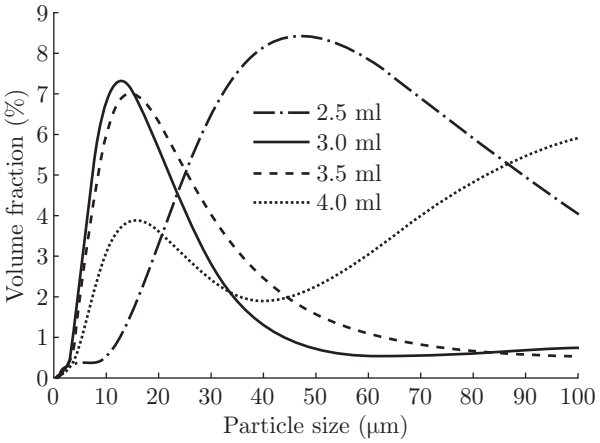


Fig. 2: The relation between particle size distribution and dosage of glutaraldehyde

It can be seen from Fig. 2 that the microcapsules with narrow particle size distribution were obtained when the amount of glutaraldehyde was of 3.0 ml. The microcapsules did not cross linked well and orderly when the amount of glutaraldehyde was of 2.5 ml. When the dosage was increased to 4.0 ml, microcapsules began to stick together and a wider particle size distribution of microcapsules was obtained. So the amount of 3.0 ml was used as the optimum parameter.

As we saw in Table 1, the highest drug-loading rate is 62.57% which coincides with the suitable amount of 3.0 ml. Using this, microcapsules were obtained with narrow particle size distribution and high drug-loading rate.

Table 1: The particle size and drug-loading rate of microcapsules with different dosage of glutaraldehyde

dosage of glutaraldehyde (ml)	mean particle size (μm)	drug-loading rate (%)
2.5	43	30.43
3.0	15	62.57
3.5	16	57.10
4.0	30	50.37

3.3 Influence of the Concentration of the Wall Materials

Five different concentration solutions of gelatin and acacia were prepared to investigate their effects on the particle size distribution of microcapsules and the results are shown in Fig. 3. The oil contents are listed in Table 2.

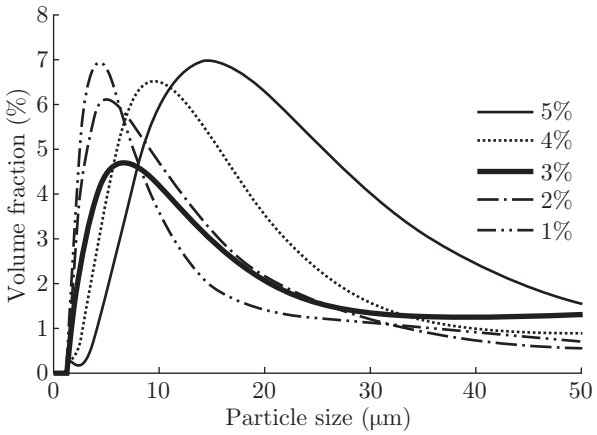


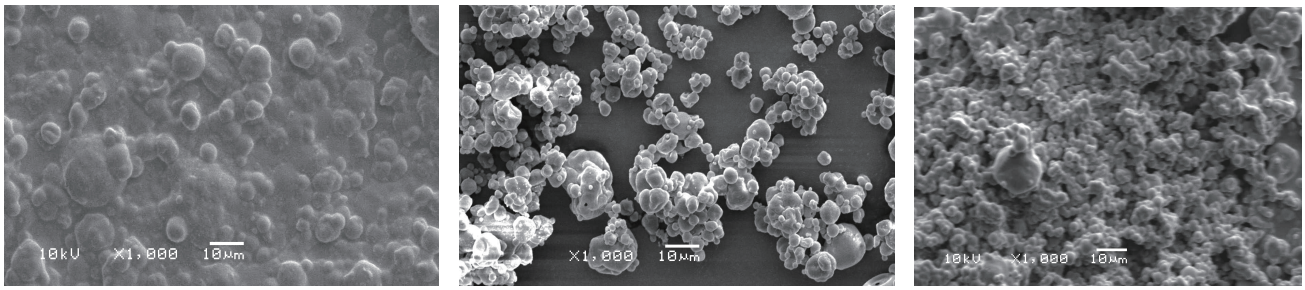
Fig. 3: Particle size distributions of microcapsules prepared at different concentrations of wall materials

Table 2: Drug-loading rate of microcapsules with different concentrations of wall materials

concentration of wall materials (%)	drug-loading rate (%)
5	62.57
4	61.99
3	62.21
2	35.98

With the increase of the concentration of wall materials from 1% to 5%, the mean particle size increased and particle size distributions became wider. The increase of the concentration of gelatin and acacia solutions may lead to a change of viscosity in the systems, and caused the microcapsules to conglutinate to a large block easily during the coacervation. The mean diameters

of microcapsules grew when the concentration increased. The data of Table 2, indicated the oil content had an adjacent value when the concentration changed from 5% to 3% and a large drop when the concentration was only 2%. It indicated 3% is critical concentrations value of wall materials during preparing the microcapsules. Above the point, we can not get good particle size distribution, and cannot obtain higher oil content microcapsules below the point. Therefore, the concentration of 3% can be taken as the optimum parameter. Scanning Electron Microscopy (SEM) micrographs of microcapsules were shown in Fig. 4.



(a) 5% (b) 4% (c) 3%

Fig. 4: SEMs of spray dried microcapsules prepared at different concentrations of wall materials

3.4 Influence of pH on Complex Coacervation

Regulation and control of the pH level during the process of coacervation is a crucial step for using complex coacervation to prepare microcapsules. When the pH in the system below the IEP of the gelatin, its positive charge attracted the acacia's negative charge, and then coacervated to form the condensed phase and wrap to the oil [11]. The Fig. 5 showed that when pH was between 3.5 and 4.5, the microcapsules prepared had small even particle size and narrow particle size distribution. When the pH of system is 4.0, particle size distribution of microcapsules was narrowest and the particle size was more uniform. The particle size increased and particle size distribution became wider when the pH was 5.0. The data of table 3 indicated that the oil content of microcapsules prepared was only 25.66% when the pH of system was 5.0. The oil content of microcapsules was up to 60.0% at the other pH values. This may arise from bad coacervation of gelatin and gum acacia at higher pH value. SEM of microcapsule prepared at pH=4.0 was shown in Fig. 6. It can be seen that the microcapsules had smooth surface and good roundness, but a portion of microcapsules existed conglutination.

Table 3: The mean particle size and drug-loading rate of microcapsules with different pH

pH	mean particle size (μm)	drug-loading rate (%)
5.0	55	25.66
4.5	12	62.21
4.0	6	60.56
3.5	10	64.76

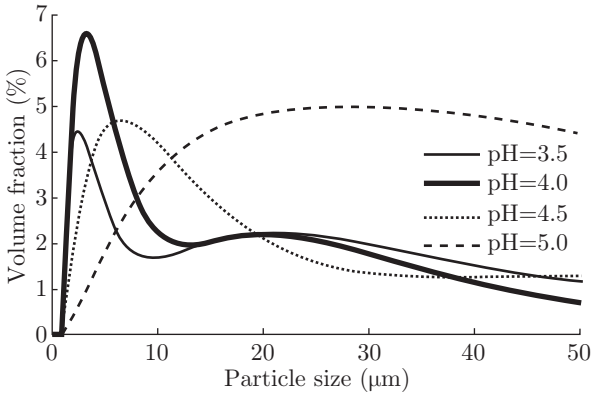


Fig. 5: The relation between particle size and pH of coacervation

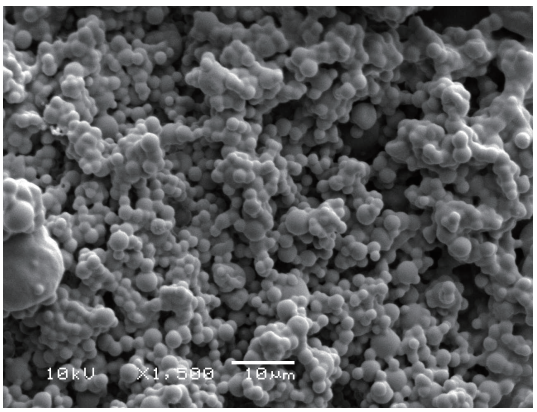


Fig. 6: Microcapsule prepared at pH=4.0 (dosage of cross linking agent is 3ml, concentration of wall material is 3%, core/wall materials is 1:1)

3.5 Influence of Core/Wall Materials Ratio

Fig. 7 was the curve of particle size and core/wall materials ratio. It can be seen from Fig. 7 that with the increase of core materials, the mean diameter of microcapsules also increases and the distribution became wider. The data of Table 4 showed that the drug-loading rate of microcapsules

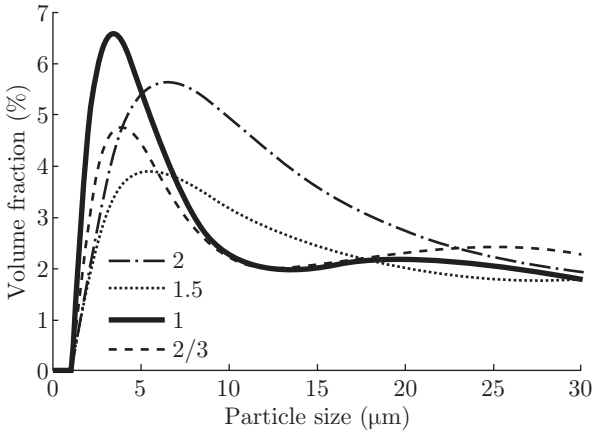
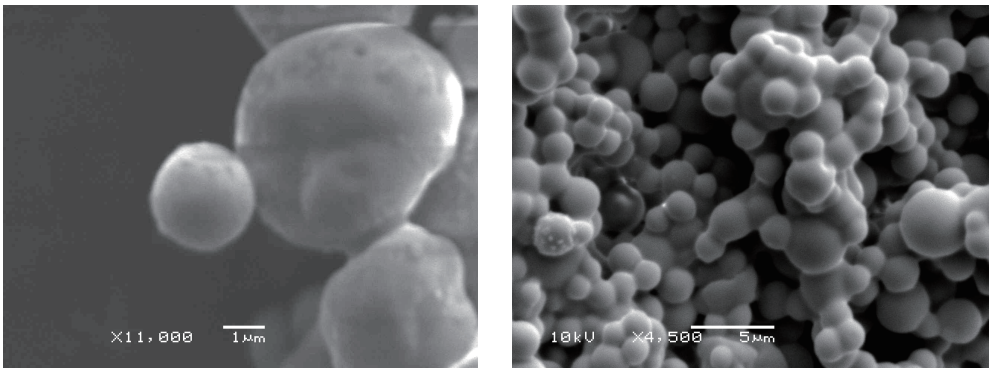


Fig. 7: The relation between particle size and core/wall materials ratio

did not change much when the core/wall ratio changed from 1:1 to 2:1. But when the core/wall ratio changed to 2:3, the drug-loading rate of microcapsules decreased to 35.92%. The relative oil content of microcapsules decreased when the amount of wall materials increased because all gelatin and gum acacia of reaction system was used to form wall of capsules in this experiment. So the capsule wall changed thicker and the particle size increased. The scanning electron micrograph of prepared at core/wall ratio=1/1 was shown in Fig. 8. It can be seen that surface of microcapsules was smooth and compact. Although there existed conglutination among microcapseles, the size of sticking microcapsules was below 10 μm.



(a) (b)

Fig. 8: SEM of microcapsule of core/wall=1:1 (dosage of cross linking agent is 3 ml, concentration of wall materials is 3%, pH of coacervation is 4.0)

Table 4: Influence of core/materials to drug-loading rate

core/wall materials	drug-loading rate (%)
2:3	35.92
1:1	60.56
3:2	62.42
2:1	64.98

3.6 Thermal Decomposition and Release Rate

A certain amount of microcapsules were put in the vacuum oven and the temperature was set up at 80℃. The quality was weighed after a period of time, until the reading became constant. The result is shown in Fig. 9, it can be concluded from the time and retention rate that the microcapsules had a fast release stage in the first 5 hours and then remained almost steady. The decomposition temperature can be determined with thermogravimetry. The results are shown in Fig. 10. It can be seen from this figure that a higher decomposition temperature microcapsules were obtained under higher concentration of wall materials. This is due to the fact that the wall materials play an important role to the heat-resistant microcapsule. Using the method of complex coacervation, the first elastic layer of microcapsule was obtained, and then the second glass layer was obtained through spray drying. The two-double wall constructures resulted in the good heat-resistant property of microcapsule. Its decomposition temperature approaches 180℃.

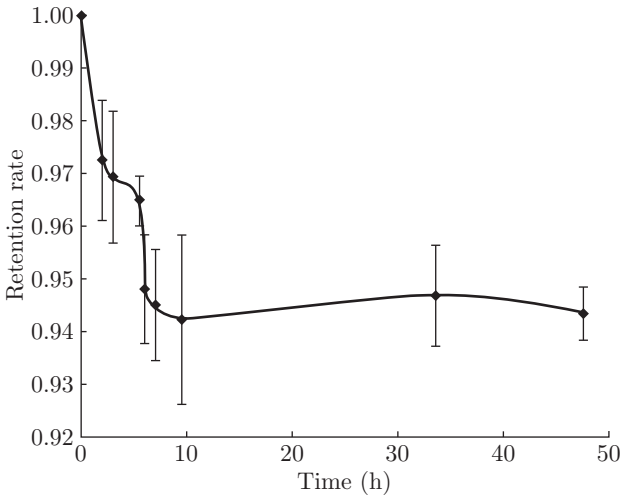


Fig. 9: The release rate of microcapsules prepared by coacervation. pH=4.0, core/wall (w/w)=1:1, Cw=3%, dosage of cross linking agent=3 ml, the stirring rate=1000 r/min, T=45℃

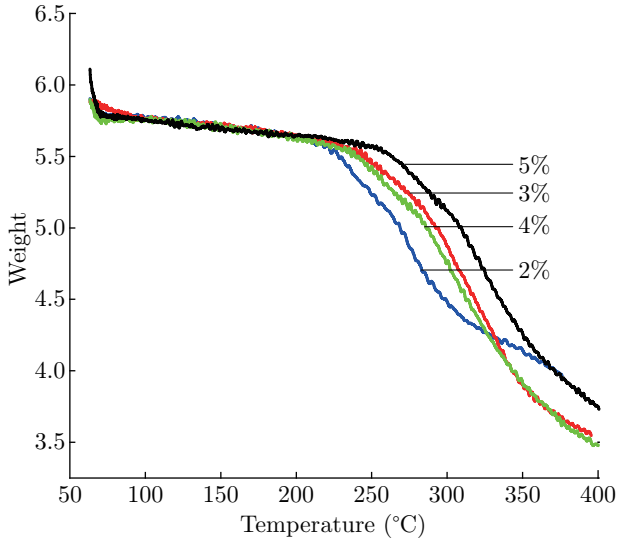


Fig. 10: Decomposition temperature of microcapsules which walls concentration are 5%, 4%, 3%, 2%, c/w=1:1, dosage of cross linking agent=3 ml, pH=4.0

4 Conclusion

Olive oil was successfully encapsulated by complex coacervation. Microcapsules prepared at appropriate cross linking agent and the suitable reaction condition had high heat-resistant performance, slow release rate and good morphology using gelatin and acacia gum as the wall materials and olive oil as the core materials, glutaric dialdehyde as the cross liking agent. The particle size distribution depends on oil content, crosslinking density, polymer concentration, etc. Thermal stability of microcapsules has been improved with the increase of wall materials in the system. The olive oil microcapsules were obtained with particle size of 3∼8 μm, oil content about 60%. The optimum process parameter were that dosage of cross linking agent is 3 ml, concentration of wall materials is 3%, pH value of coacervation is 4.0 and the ratio of core/wall material is 1:1. Olive oil microcapsules prepared at optimal process condition had good disperse and high

encapsulation efficiency.

The main aim of preparing olive oil microcapsule was to produce functional fabric by spinning or coating. And the fabric can let the skin glossy and soft and remove fatigue.

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