ISSN:2790-1688 DOI: 10.56028/aetr.3.1.704

Preparation and properties of n-hexane microcapsules by complex coacervation

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Abstract. In order to improve the encapsulation efficiency of low density core material microcapsules, the complex condensation method was used to prepare microcapsules with n-hexane as the core material and gelatin and Arabic gum as the wall material.For n-hexane with low density, the influence of wall material concentration on microcapsule morphology, the influence of core wall ratio on microcapsule wall thickness, the influence of emulsifying speed on emulsifying effect, the influence of crosslinking curing reaction pH on thermal stability, and the influence of complex coacervation pH on turbidity were studied by turbidimetric titration. The experimental results show that: For the low-density core microcapsules, the spherical multi-core microcapsules prepared are regular in capsule shape, but the encapsulation efficiency is lower than 30%, and the waste of wall material is serious. The wall material concentration is 2%, the core-to-wall ratio is 3:1, the emulsification speed is 10000 r/min, the pH of complex oacervation is 4.0, and the pH of crosslinking curing reaction is 10.0. The microcapsules prepared on this basis are monocytic and irregular. Although the shape and phase of the capsules are irregular, they have good encapsulation effect, with the yield up to 71.86% and encapsulation efficiency up to 70%. Meanwhile, they have good thermal stability.

Keywords: microcapsule; complexcoacervation; turbiditytitration; glutaraldehyde

1. Introduction

There are many common preparation methods of microcapsules, such as spray drying [1], interfacial polymerization [2], in situ polymerization [3], complex coacervation [4] and so on. The complex coacervation method has the characteristics of high efficiency and high yield for wrapping insoluble liquid and solid powder. Gelatin and acacia are protein and polysaccharide respectively, which are the classic wall material combinations for the preparation of microcapsules by complex coacervation method. The wall material has the characteristics of green, non-toxic and easy biodegradation. N-hexane has a density of 0.66g/cm3, which is insoluble in water, volatile and has a special smell. It has a low boiling point and does not react with wall material, making it an ideal core material for research. In this paper, n-hexane as the core material, gelatin and gum acacia as the wall material, study the factors affecting the preparation of microcapsules by complex coacervation method, improve its encapsulation efficiency, and play a theoretical and practical guiding role in the preparation of microcapsules by complex condensation method for oily materials with lower density.

2. Experiments

2.1 Materials

Gelatin. Gum Arabic, n-hexane. Glutaraldehyde were provided from Shanghai Titan Technology Co. Ltd.China.All chemicals were of analytical grade and were used without further purification. Deionized water was used for all experiments.

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2.2 Preparation and Characterization of the Microcapsule

The preparation process of microcapsules is shown in Fig 1.The specific steps are to configure gelatin and gelatin solutions of 2% concentration respectively.Add 24g of n-hexane into the gelatin solution and emulsify it at a speed of 10000r/min with digital display at 40℃ for 2 minutes. Then pour it into a jacketed flask and stir it with agitator at a speed of 600r/min. Then add the acacia solution and adjust pH=4.0. Reduce the temperature to 10℃ for reaction for 1 hour, then add glutaraldehyde, adjust pH=10, reaction for 2 hours, and then through filtration, drying to obtain microcapsules.

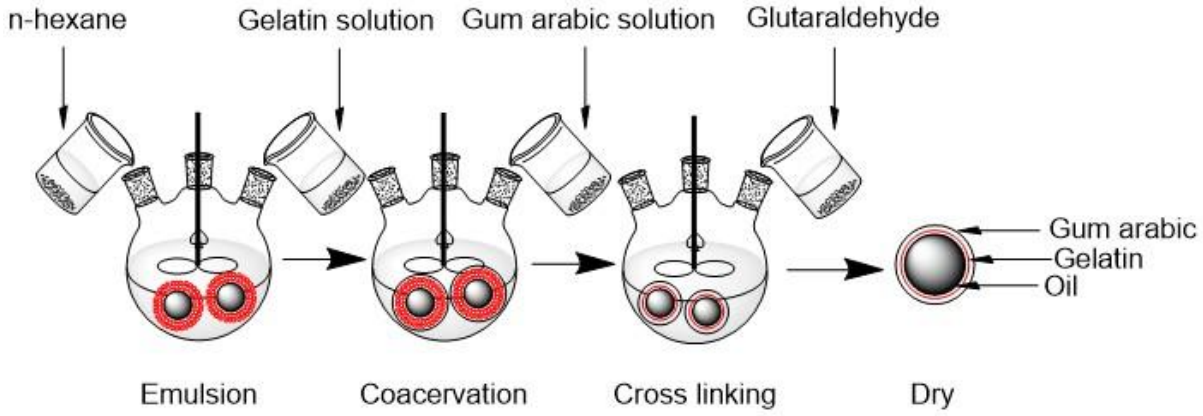

Fig.1 The preparation process of microcapsule

2.3 Microcapsule Drying

The microcapsule suspension was extracted and filtered by vacuum extraction and filtration device, and the extraction and filtration products were placed into the electric blast drying oven (Shanghai Lichen Bangxi Instrument Technology Co., LTD.). The drying temperature was set at 60℃, and the microcapsules were collected after drying for further study.

2.4 Microcapsule Morphology

The surface morphology of microcapsules was observed by optical microscopy 9XB-PC (Shanghai Optical Instrument Factory China).

2.5 Turbidity Measurement Conditions

Turbidity of the biopolymer mixtures was measured at 600 nm using a spectrophotomerer(UV-3600, Shimadzu Corporation of Japan) with cuvettes of 1 cm light path. The solution concentration is 5×10^{-4} g/ml.

2.6 The Rmogravimetric Measurements

Using synchronous thermal analyzer STA409PC (Nexe, Germany), microcapsule samples in nitrogen environment, temperature measurement range of 20-300 ℃, heating rate of 10 ℃/min.

2.7 Determination of Microcapsule Properties

In this paper, the ratio of the dried microcapsule mass to the initial wall material and core material was used to calculate the capsule yield. The encapsulation efficiency is calculated by the ratio of microcapsule core material mass to microcapsule mass.

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3. Results and Discussion

3.1 Effect of Wall Material Concentration on Microcapsule Morphology

The morphology of microcapsules under different wall material concentrations is shown in Fig 2. When the wall material concentration is 1%, the microcapsules are spherical and multinucleated with regular cystic shape, but the density of n-hexane is 0.66g/cm3, which is relatively small. The microcapsules precipitate at the bottom of the solution， The results showed that the encapsulation efficiency of microcapsules was low due to the small amount of encapsulated core material. And the amount of wall material and core material is small, so the solid content in the solution is low, the production efficiency is low, which is not conducive to industrial production. When the concentration of wall material increased to 2%, the microcapsules changed from spherical multi-core to irregular single-core, pepod-like shape, although the shape was irregular, but the coating effect was still good. When the concentration of wall material continues to increase to 3%, effective coating cannot be formed due to the high viscosity of condensed phase, and the embedding effect decreases instead. The experimental results show that when the wall material concentration is 2%, the coating effect is good and the encapsulation efficiency is high.

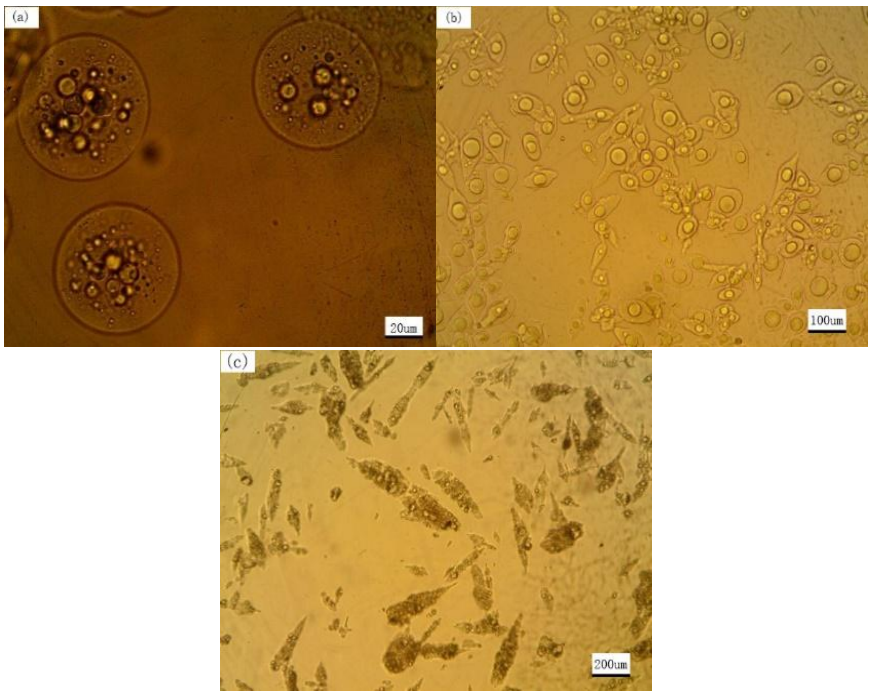

Fig.2 Effects of different wall material concentrations on microcapsule morphology:(a) 1wt%(b) 2wt%(c)3wt%

3.2 Effect of Core-To-Wall Ratio on Microcapsule Wall Thickness

The influence of different core-to-wall ratios on microcapsule wall thickness is shown in Figure 3. When the core-to-wall ratio is low, the microcapsule wall is thicker, the coated core material is less, and the yield and encapsulation efficiency are lower. With the increase of core-to-wall ratio, the microcapsule wall becomes thinner, the coated core material droplets become larger, and the microcapsules float on the top of the solution. The yield and encapsulation efficiency also become larger, but the excessively large core-to-wall ratio makes the capsule wall thinner and leads to poor stability. The experimental results show that when the core-wall ratio is 3:1, microcapsules have high strength, high yield and encapsulation efficiency.

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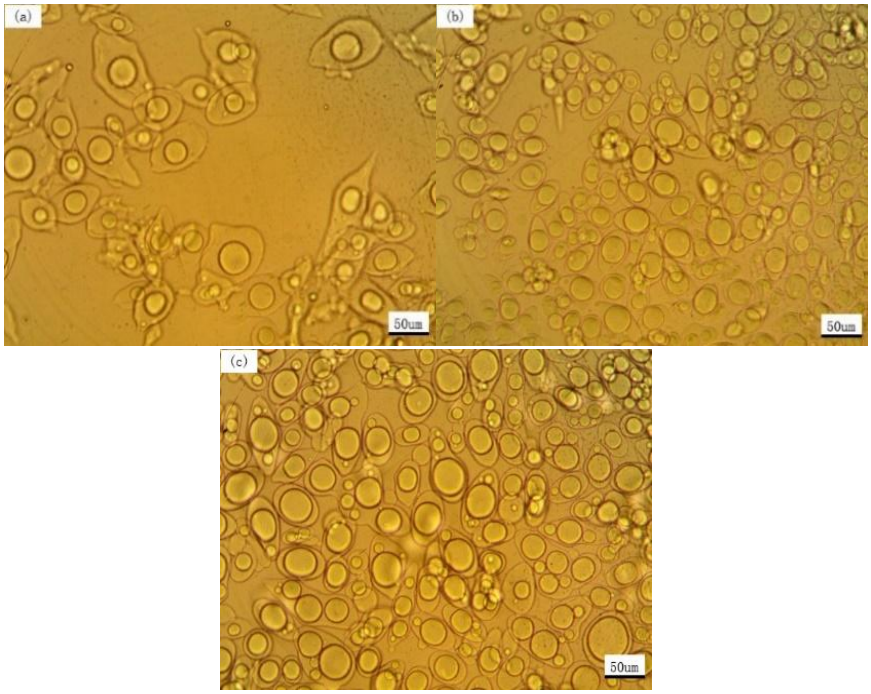

Fig.3 Effect of core-to-wall ratio on microcapsule morphology:(a) 1:1(b) 2:1(c)3:1

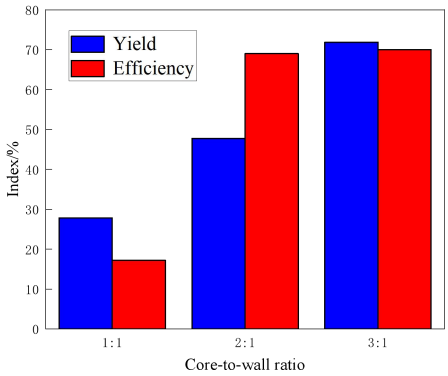

Fig.4 Effect of core-to-wall ratio on yield and efficiency

3.3 Influence of Emulsifying Speed on Emulsifying Effect

The oil-water interface has high interfacial energy, which usually requires stirring to break the bondage of interfacial tension and form o/w lotion. Therefore, the stirring speed is an important parameter affecting the characteristics of lotion [5]. It can be seen from table 1 that emulsification at different speeds has a significant impact on the encapsulation efficiency of microcapsules. High speed emulsification can improve the emulsifying effect and obtain higher encapsulation efficiency. In addition, the extension of emulsifying time did not make up for the speed gap and improve the emulsifying effect. It can be seen from Fig 5 (a) that the particle size of lotion is large and the particle size distribution is uneven at the speed of 650r/min, so it is difficult to form a stable lotion, while the particle size of lotion formed at 10000r/min in Figure 5 (c) is small and the particle size distribution is uniform. Smaller particle size has a relatively larger specific surface area, and gelatin molecules are easier to adhere to it to form a stable lotion, thereby improving the encapsulation efficiency.

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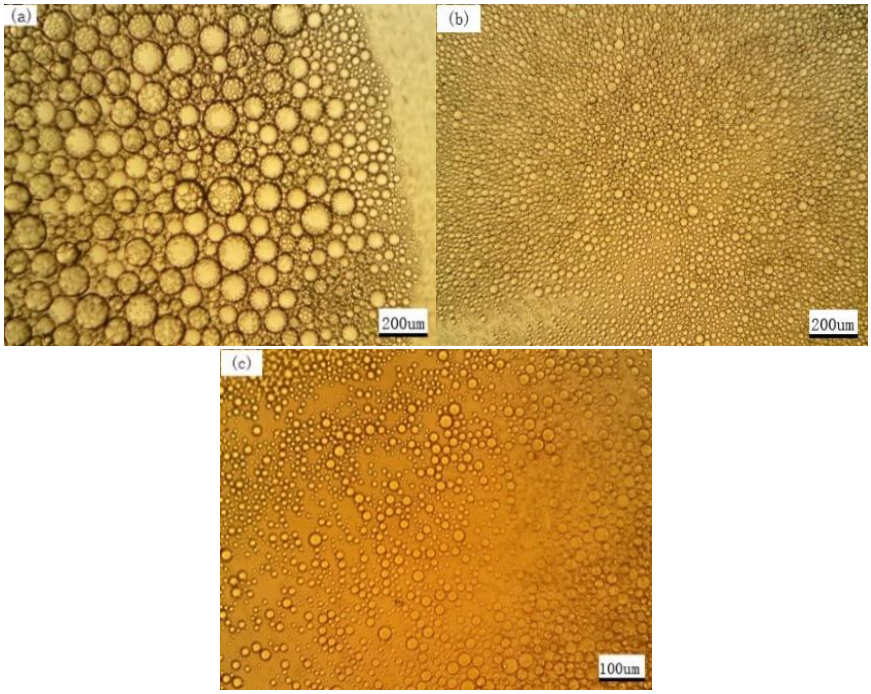

Fig.5 Effect of rotational speed on droplet morphology of emulsion:(a) 600r/min(b) 2000r/min(c) 10000r/min

Table1.Effect of emulsifying speed on microcapsule performance

wall material concentrations /%	core-to-wall ratio	temperature /℃	speed/rpm	time/min	efficiency/%
2	3	40	600	30	54.4
2	3	40	2000	30	61.23
2	3	40	10000	2	70

3.4 Effect of Ph of Complex Coacervation on Turbidity

Complex coacervation is usually defined as the aggregation phenomenon formed by electrostatic interaction of two substances with opposite charges [6], and the reaction product is called complex condensate. When the pH of gelatin solution is lower than its isoelectric point, it is positively charged, while Arabic gum is anionic polysaccharide with negative charge. Based on this principle, there must be an electrostatic equilibrium pH value. At this time, gelatin and Arabic gum have opposite charges, the absolute value of the charge is equal, and the complex condensation reaction product is the largest [7]. At present, the most commonly used methods to determine the optimal pH of complex coagulation reaction are potentiometric method [8-9], turbidity titration method [10-12], laser light scattering method [13], etc. In this paper, turbidity titration is used to determine the pH of complex coagulation reaction. The basic principle of turbidimetric titration is that when the complex condensation reaction occurs to form the complex condensate, the turbidity of the solution will change. When the complex condensation reaction product is the largest, the turbidity of the solution will also reach the maximum value. Using ultraviolet visible near infrared spectrophotometer UV-3600,calculate the turbidity according to the following formula:

$$\tau = -\left(\frac{1}{L}\right) ln\frac{I}{I_0} \quad (1)$$

among τ is turbidity, L is the length of light path (cm), I is the radiation intensity transmitted through the biopolymer mixture in the specific tube,I0 is the incident radiation intensity, where I to I0 is the transmittance[14]. According to the formula, the turbidity can be calculated, and the change curve of turbidity under different pH can be obtained, as shown in Fig 6. When ph=4.5, the turbidity of the solution system is still very small, indicating that the complex condensation reaction has just occurred. With the continuous reduction of pH, the turbidity is getting larger and larger,

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indicating that the complex condensation reaction is getting stronger and stronger. When ph=4.0, the turbidity reaches the maximum value, indicating that the electrostatic equilibrium value has been reached at this time, that is, the complex condensation reaction product reaches the maximum value. When the pH is further reduced, the turbidity has begun to decrease. Therefore, it can be determined that when the ratio of gelatin to Arabic gum is 1:1, the optimal pH of the complex coagulation reaction is 4.0.

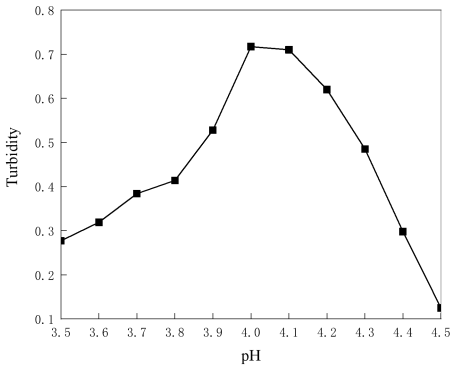

Fig.6 Influence cure of pH on turbidity of solution

3.5 Influence of Ph on Thermal Stability of Crosslinked Curing Reaction

The strength and thermal stability of microcapsules can be enhanced by crosslinking curing reaction. Transglutaminase [15] and aldehydes, such as formaldehyde [16] and glutaraldehyde [17,18], are usually used as crosslinking agents. The principle of crosslinking curing reaction between gelatin and glutaraldehyde is shown in Fig 7.There are a large number of amino groups on gelatin, The carbonyl group of glutaraldehyde can react with the amino group of gelatin, cross-linking the amino groups on the gelatin chain to form a network of polymers, to achieve the effect of curing. According to the properties of gelatin, amino group will ionize under acidic conditions and form cation -NH3+, which is not easy to crosslink with aldehyde group. Therefore, crosslinking reaction between amino group and aldehyde group is usually carried out under alkaline conditions [19].

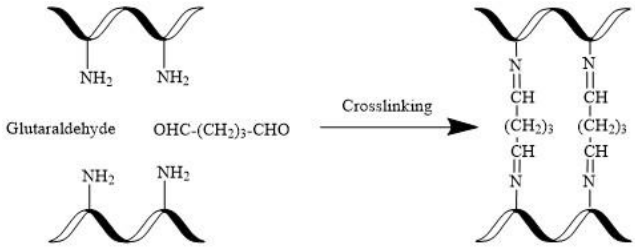

Fig.7 Principle of gelatine and glutaraldehyde crosslinking curing reaction

In the experiment, 0.05% glutaraldehyde was used as crosslinking agent, Crosslinking reaction was performed at pH=8, pH=9 and pH=10 respectively. After the reaction, microcapsules were obtained by filtration and drying. 10g microcapsules prepared under the above three conditions were respectively placed in an electric blast drying oven and heated at a constant temperature of 80 ℃ for 10 hours. Mass fraction was recorded for each hour and plotted as a curve, as shown in Fig.8. The microcapsules prepared by crosslinking reaction at pH=10 had the slowest change in mass fraction, which was higher than those prepared by crosslinking reaction at pH=8 and pH=9 in each time period, indicating that they had better heat resistance. The three groups of samples, which were dried for 10 hours at 80 ℃, were heated to 200 ℃ for 1 hour, so that the capsules were completely broken and the core material was completely drained. The final weight loss of microcapsules prepared by crosslinking reaction at pH=8 was 73.32%,at pH=9 was 76.48% at pH=10 was 76.92%, respectively. It can be seen that the microcapsules prepared under the three

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conditions have no obvious difference in coating effect, but they have better heat resistance under the condition of pH=10. Therefore, the pH selected for cross-linking reaction is 10.

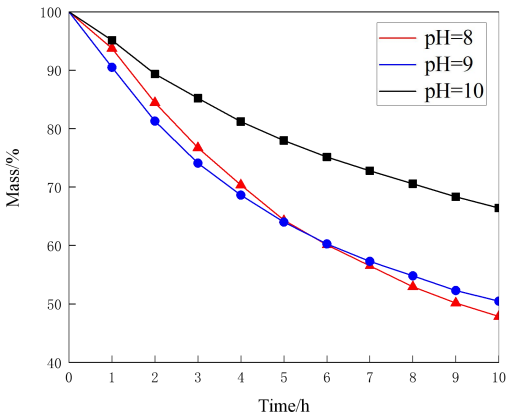

Fig.8 The mass fraction change curve of microcapsules prepared by crosslinking at diffferent pH at 80℃

3.6 Heat Release of Microcapsules

Fig.9 shows the thermogravimetric curve of microcapsules and its derivative curve. The thermogravimetric curve is approximately a parabola and can be divided into four stages for analysis. In the first stage, the temperature rises from 20 ℃ to 100 ℃, and the weight loss is about 9%. In this stage, the weight loss is mainly the evaporation of water and the encapsulation of microcapsules with poor effect. In the second stage, the weight loss from 100 ℃ to 160 ℃ is about 14%, which is the slow release of the inner core material of the microcapsule. In the third stage, from 160 ℃ to 240 ℃, the weight loss of microcapsules is about 41%. It can be seen that the weight loss of microcapsules is severe at this stage. From the derivation curve, it can be seen that the maximum weight loss of microcapsules under heating at about 200 ℃.The fourth stage is from 240 ℃ to 300 ℃, and the weight loss in this stage is about 6%. It can be seen that the curve is nearly stable at this time, indicating that the core material has completely volatilized at this time, and the slight weight loss is due to the decomposition of the wall material at high temperature.The boiling point of n-hexane is 69 ℃. It can be seen from the above analysis that n-hexane has been successfully coated and microencapsulated, showing good heat resistance.

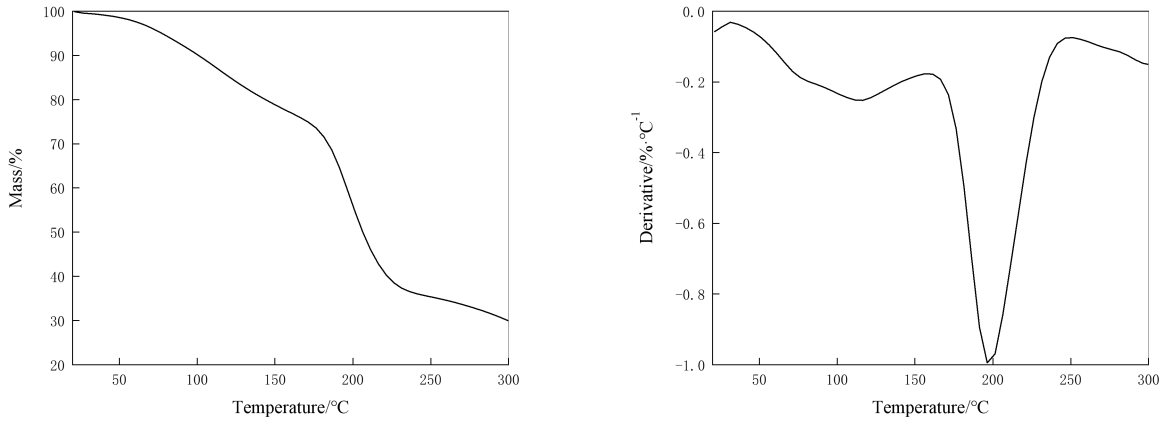

Fig.9 Thermogravimetric curves of microcapsules and their derivatives

4. Conclusion

This experiment on the compound condensing the influence factors of the preparation of

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microcapsule is studied, including wall material concentration and core wall than can be combined with the actual requirements to choose the appropriate parameters, considering the n-hexane core material density is small, there is no common wall material concentration 1%, core wall than 1:1 under the condition of the preparation of microcapsule, but is optimized on the basis, the process conditions were determined: Wall material concentration 2%, core-to-wall ratio 3:1,emulsification speed 10000r/min complex condensation reaction pH=4.0, crosslinking curing reaction pH=10.0.

Microcapsules are mainly mononuclear irregularly shaped, similar to pods, and their yield and encapsulation efficiency can reach 71.86% and 70%. Through optical microscope and thermogravimetric analysis, it can be seen that the core material is successfully coated with good thermal stability.

Acknowledgments

This project was financially supported by the National Natural Science Foundation of China (No.52005315).

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