

Preparation and Characterization of Microcapsules Containing Capsaicin

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ABSTRACT: With urea-formaldehyde (UF) resin as walls and capsaicin as core substances, microcapsules were prepared based on *in situ* polymerization process. The morphology and size distribution of the microcapsules were analyzed by Fourier transform infrared spectroscopy, laser particle size analyzer, and scanning electron microscopy. The microcapsulated capsaicin (MC) agents had a mean diameter of about 30–50 μm . Moreover, the thermal properties of the MC agents were measured by differential scanning calorimetry and thermogravimetric analysis. It was demonstrated that the melting point and thermal sta-

bility of the MC agents were greatly improved compared with that of the uncovered capsaicin, which were caused by the encapsulating crosslinked UF resin over the surface. The shell formation mechanism and the effects of the process conditions such as U/F ratio, shearing force, and acidification time on the particle size of the MC agents were discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2234–2241, 2010

Key words: capsaicin; urea-formaldehyde resin; microencapsulation; morphology; properties

INTRODUCTION

Capsaicin is the common name for 8-methyl-*N*-vanillyl-*trans*-6-nonenamide. This material is most well known for its inhabitancy in the internal white ribs of chili peppers and its ability to produce the burning hot sensation of chili-laced spicy foods. Capsaicin has a naturally occurring pungent odor that could prevent small animals, such as microbes, insect and mouse, from attaching to polymer materials while being benign to the environment.^{1,2}

However, capsaicin has the shortcomings in the following aspects: first, the intensively pungent odor is not comfortable for the operator in the applied process; second, its efficiency will decrease for its quick release properties in a given environment.

The encapsulation of the capsaicin could avoid these problems. Microencapsulation is a process of enveloping microscopic amounts of matter in a thin

film of polymer.^{3,4} This shell/core structure allows isolation of the encapsulated substance from the surroundings. The polymer materials can keep stable before the shell is destroyed. The encapsulated substance can be liberated by fusion or dissolution of the impermeable shell or by diffusion across a porous shell.^{5,6}

The study of encapsulation of the capsaicin with polymeric materials shell, urea-formaldehyde (UF) resin, may have following two reasons. First, we can expect that the microcapsules with this shell will be compatible with the applied polymer matrix. Second, UF resin is a good candidate for preparation of microspheres and microcapsules for the purpose of controlled release of drugs.

Yi et al.⁷ synthesized different microcapsules containing an organic solvent as an internal phase by *in situ* polymerization of UF resin without prepolymerization. Cosco⁸ researched the physical properties of UF microcapsules containing an epoxy resin. Park et al.⁹ prepared UF microcapsules by *in situ* interfacial polymerization to lemon oil as the core material. UF resin types were investigated for their effects on thermal properties, mean particle size, and size distributions. Till now, the preparation of microcapsulated capsaicin (MC) using UF resin has not been researched.

In this work, a type of microcapsule containing capsaicin was synthesized by *in situ* polymerization with UF resin. Initially, we described the preparation of capsaicin coated by UF resin using a prescribed

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method. Then, the morphology, size distribution, and thermal properties of the MC agents are characterized by a Fourier transform infrared (FTIR), laser particle size analyzer, scanning electron microscopy (SEM), differential scanning calorimeter (DSC), and thermogravimetric analysis (TGA). Lastly, the shell formation mechanism and the factors that influence the particle size of the MC agents were discussed.

EXPERIMENTAL

Materials

To prepare these MC agents, capsaicin was supplied by Tianjin Yirui Food Company (Tianjin, China). Absolute urea, formaldehyde, sodium hydroxide, and glacial acetic acid were of analytical grade. These agents were supplied by Shanghai Guoyao Agent Company (Shanghai, China).

Preparation of MC agents

The method used for preparing these MC agents was *in situ* polymerization. The following procedure was used to prepare these agents: 10 g of urea was poured into a four-necked flask, and 10–30 g of formaldehyde was added in, respectively. The system was cured for 0.5 h after heating to 70°C. Then, the pH value was adjusted by sodium hydroxide until the system turned to milky white. Capsaicin (15 g) and water (60 g) were dispersed in the above solution, and then it was stirred for 0.5 h. Glacial acetic acid (30 mL) was poured into the above system, and the pH value was adjusted to 1.5. Then, it was maintained for 30–90 min. The resulting agents were rinsed several times by distilled water, and then placed in a vacuum oven at 50°C for 12 h to dry. The dried cake was ground to obtain the agents.

Characterization of MC agents

FTIR spectroscopy

FTIR spectra of the surface functional groups of capsaicin and MC agents were recorded on a Nicolet Avatar 370 Fourier transform infrared spectrophotometer in the range 4000–700 cm^{-1} at a resolution of 2 cm^{-1} . Samples were ground and mixed with KBr to form pellets. Sixty-four scans were necessary to obtain spectra with good signal-to-noise ratios.

Particle size and distribution

The particle size and distribution of MC agents were analyzed by a laser particle size analyzer (model Psl.rfd PIDS included, Beckman Coulter Corp.). The particle size analyzer was equipped with a measurement cell. A lens capable of detecting particles in the

size range of 0.01–80 μm was attached to the optical measurement unit. For the protection of the analyzer, aggravating liquids were avoided and only mild liquids, such as ethanol, were used for dispersing the capsaicin and the MC agents.

Photographs and scanning electron microscopy

Photograph of the MC agents was taken by a digital Sony camera. SEM analysis of the capsaicin and MC agents was carried out using Comscan Series 4 instrument. The samples were gold coated using an IB-3 Ionic sputtermeter.

Transmission electron microscopy

TEM analysis of the microcosmic morphology of the MC agents was carried out by a Hitachi H-800 instrument using an acceleration voltage of 100 kV. The samples were dispersed in ethanol with the assistance of ultrasonic bath agitation, and then deposited on a copper grid for TEM observation.

Thermal analysis

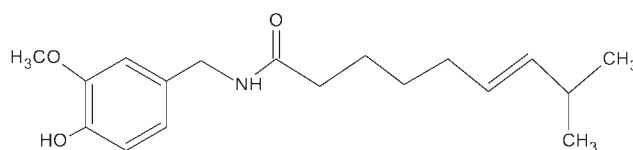
The heat of fusion and melting temperature of the capsaicin and the MC agents was obtained with a DSC 5SC/580 from Seiko Instrument and Electronics Ltd. TGA was carried out at 10°C/min under air (flow rate $5 \times 10^{-7} \text{ m}^3/\text{s}$, air liquid grade) using a Universal V4.2F TA microbalance. In each case, the mass of samples used was fixed at 10 mg and the samples (powder mixtures) were positioned in open vitreous silica pans. The precision of the temperature measurements was 1°C over the whole range of temperatures.

RESULTS AND DISCUSSION

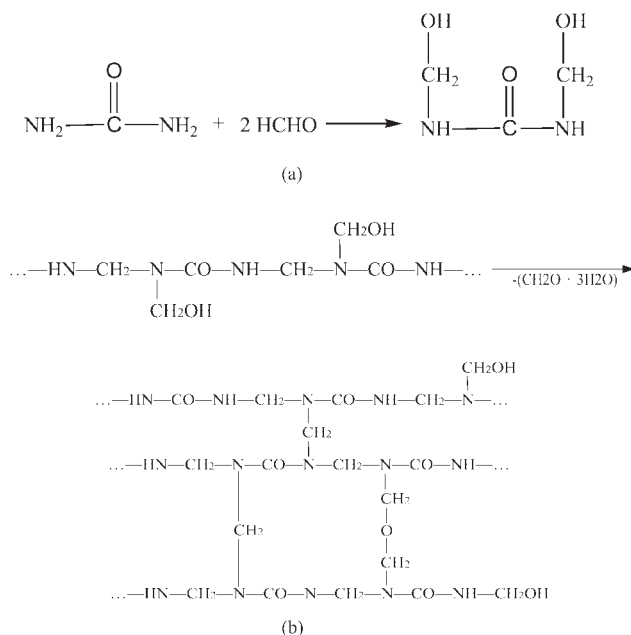
Structure analysis of MC agents

FTIR spectra of the capsaicin and MC agents are shown in Figure 1(a) and (b). It is observed from Figure 1(a), the capsaicin spectrum, that there are three obvious absorption peaks at 3350, 2900, and 1050 cm^{-1} . These correspond to the stretching vibrations of $-\text{OH}/-\text{NH}$, $\text{C}-\text{H}$ and $\text{C}-\text{O}-\text{C}$ presented in the capsaicin. Its chemical formula is shown in Scheme 1.

Scheme 2 presents the suggested reaction mechanism of urea and formaldehyde. Dimethylol urea is



Scheme 1 Chemical formula of capsaicin.



Scheme 2 (a) Development of dimethylol urea; (b) Development of crosslinked shell materials.

the main substance that produced during this alkaline environment by the addition of sodium hydroxide. The chemical formula is shown in Scheme 2(a). Scheme 2(b) shows formation of the crosslinked microcapsules shell.¹⁰ In the spectrum of the MC agents that is shown in Figure 1(b), the main absorption peaks appear at 3300, 1650, and 1250 cm^{-1} . The characteristic absorptions at 3300 cm^{-1} result from the stretching vibrations of $-\text{OH}$ and $-\text{NH}$ groups. The obvious absorption peaks between 1600 and 1630 cm^{-1} correspond to the stretching vibrations of amide group, whereas the absorption peaks at 1300

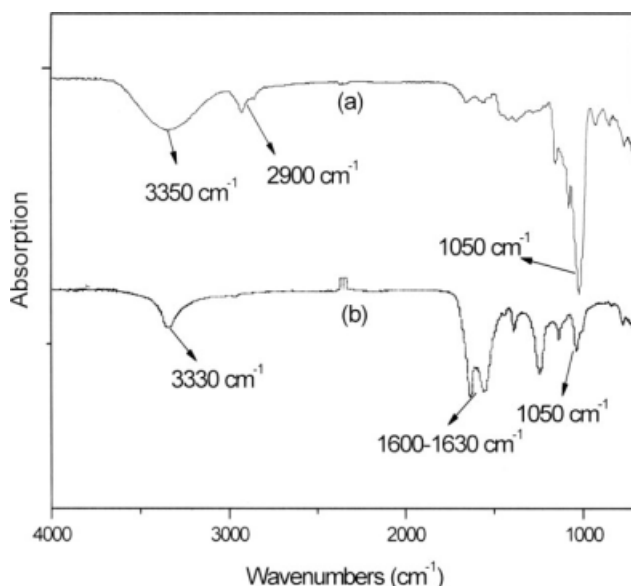


Figure 1 FTIR of (a) capsaicin; (b) MC agents.

cm^{-1} are ascribed to the absorption peaks of C—N group. The absorption peak at 1050 cm^{-1} weakens obviously, which in some extent, can illustrate that the capsaicin was well encapsulated by UF resin.¹¹

Morphology analysis of MC agents

Photograph of the MC agents is shown in Figure 2. From this figure, we can see that these MC agents are pale yellow powders that are congregated together. Little pungent odor can be smelled which demonstrates that they are well encapsulated by UF resin.

The microscopic morphology of the capsaicin and MC agents was supported by SEM photomicrographs. This is shown in Figure 3. As evidenced by Figure 3(a) and (b), the capsaicin and MC agents had a particle size about 30 μm . We can see from Figure 3(a) that the capsaicin aggregated together. This was due to the strong interactions between the molecules of capsaicin. From Figure 3(b), we can see that the MC agents had good spherical geometry, and they separated obviously from each other. This may be caused by the decreased surface tension and less interactions between each MC agent.

Particle size distribution of MC agents

The particle size distribution of the capsaicin and MC agents is shown in Figure 4. The analysis showed a polydispersed size distribution for both. From Figure 4, we can know that the average diameter of the capsaicin was between 15 and 30 μm . With the addition of UF shell to the surface, the effective diameter of the MC agents increased to 30–50 μm . This is in good accordance with the results of SEM analysis.

Thermal analysis of MC agents

The thermal property of microcapsules containing capsaicin was evaluated using DSC. DSC curves of

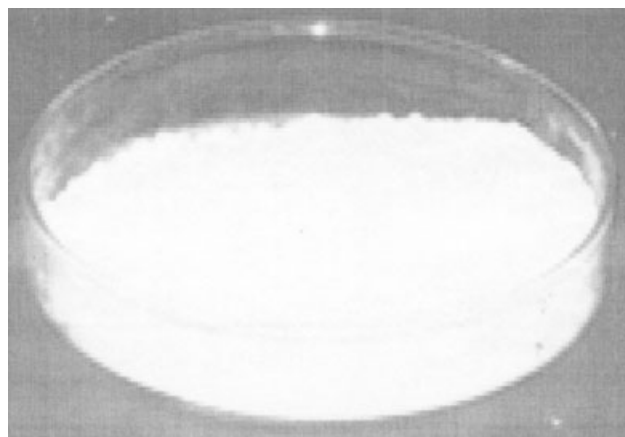


Figure 2 Photograph of MC agents.

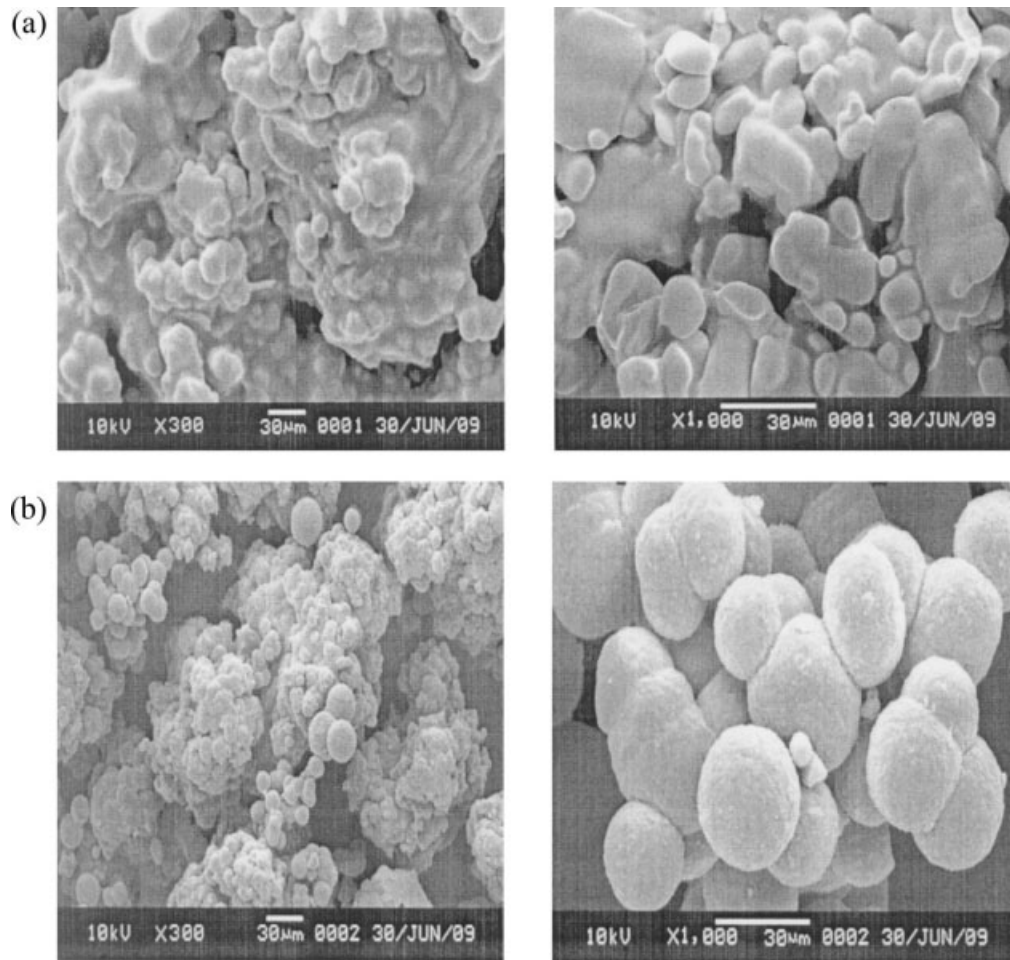


Figure 3 SEM of (a) capsaicin; (b) MC agents.

the capsaicin and MC agents are presented in Figure 5. The core material, capsaicin, used in our experiments melts at 75°C (T_m) and absorbs 160.7 J of heat per gram. With encapsulation of UF resin to the system, it is noted that the T_m was increased to 117°C

and absorbs 205.8 J of heat per gram. This is caused by the crosslinked UF resin over the surface. Also from Figure 5, we can know that the MC agents show a phase change over the temperature range 75–150°C.

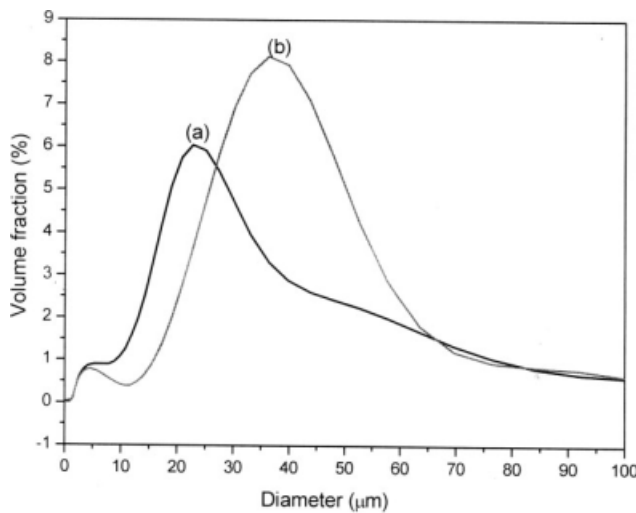


Figure 4 Particle size distribution of (a) capsaicin; (b) MC agents.

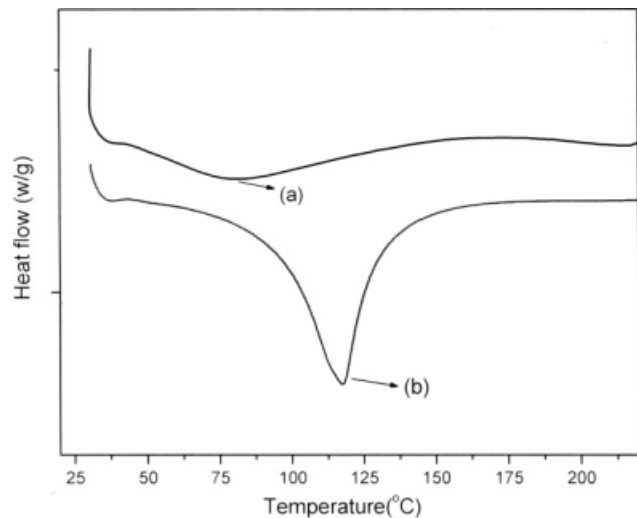


Figure 5 DSC of (a) capsaicin; (b) MC agents.

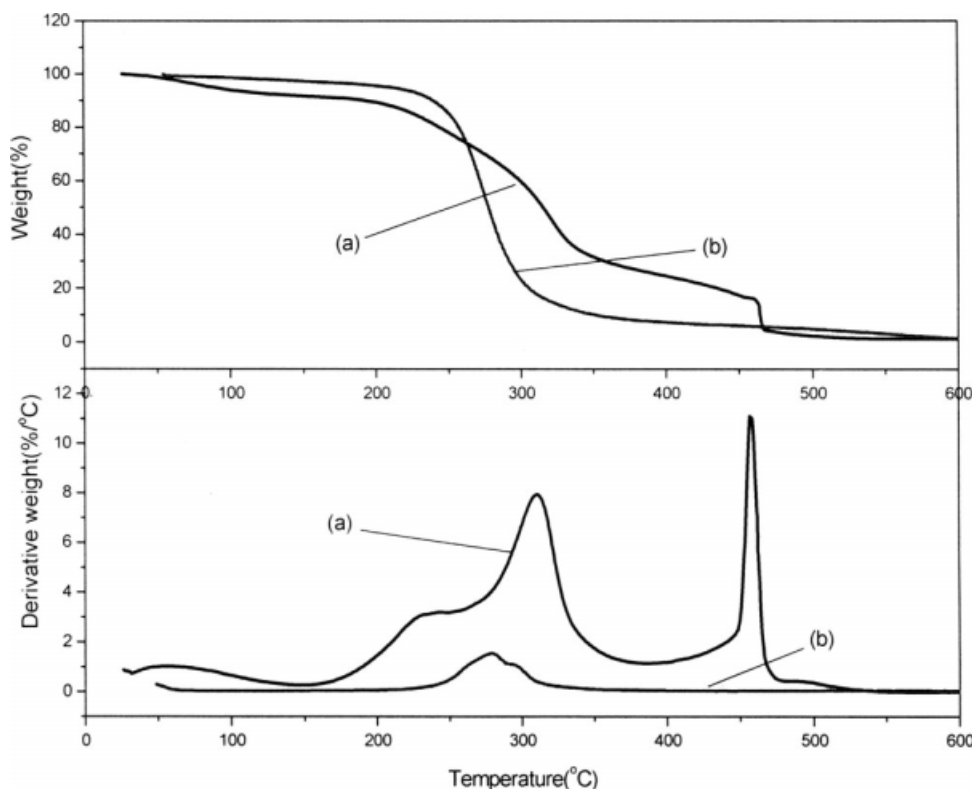


Figure 6 TGA curves of (a) capsaicin; (b) MC agents.

TGA curves of the capsaicin and MC agents are presented in Figure 6. The MC agents had a relatively enhanced thermal behavior in comparison with that of the capsaicin.

The capsaicin is a kind of amide, and the thermal stability of which is relatively poor. Three degradation steps can be seen from Figure 6(a). The capsaicin firstly shows initial weight loss at 150°C and shows the highest degradation degree at 230°C. This may be due to the rupture and degradation of the amide group in the capsaicin. The second step starts at 250°C and degrades intensively at 310°C. This can be ascribed to the decomposition of the alkene and methyl group in this material. The third step starts at 390°C and shows highest degradation at 450°C. This may be deduced to the hydrolysis of the remaining organic compounds in the residue.

Figure 6(b) shows TGA study under air of the MC agents we synthesized. It demonstrates that thermal stability of the capsaicin is greatly improved after crosslinking reaction. Its degradation under air occurs in only one step. This step starts at about 250°C. This has something to do with the degradation of the crosslinked UF resin. This step shows the highest degradation at about 285°C. From these figures, we also can see that the intensive degree was decreased after encapsulation of UF resin on the surface of capsaicin.

As a conclusion, the overall thermal stability of capsaicin was improved. This is beneficial for the application of capsaicin in the fields, such as plastics and rubber, which require high operating temperatures. However, a decrease of remaining weight between 270 and 460°C after microencapsulation,

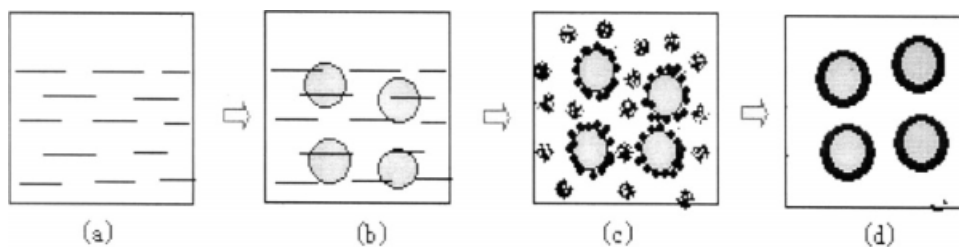


Figure 7 Formation process of MC agents.

TABLE I
Influence of U/F ratio on the Morphology of MC Agents

U/F ratio	Phenomenon
1 : 1.1–1.3	No microcapsules
1 : 1.4–1.7	Microcapsules with globular shape
1 : 1.8–2.0	Microcapsules with irregular shape

which in some extent, can influence its application, and this needs further consideration and deeper research.^{12–14}

Mechanism of shell formation

The *in situ* polymerization of microcapsule shell formation may conform to the following process as shown in Figure 7. Figure 7(a) shows the step of addition reaction between the shell material urea and formaldehyde. Dimethylol urea is the main substance that produced during this alkaline environment by the addition of sodium hydroxide. Figure 7(b) illustrates the dispersion of capsaicin in the above solution. Figure 7(c) depicts the coacervation and development of shell materials on the surface of capsaicin. Figure 7(d) may result from the possible

formation of crosslinked microcapsules shell by addition of acetic acid.

In this study, UF resin encapsulated capsaicin was prepared by above *in situ* polymerization technique. The shape and size of the microcapsules were dependent mainly on the process conditions, such as the ratio between urea and formaldehyde, shearing force, and acidification time.

A well-known relationship between the diameter of the particle size, d , and the vessel geometry together with the physical properties of the dispersion system is described by following equation.¹⁵

$$d = b(1 + c\varphi)(N_{We})^{-0.6} \cdot D_I \quad (1)$$

where $N_{We} = \rho_c(N^*)^2 D_I^3 / \sigma$ is the Weber number of the main flow, D_I is the diameter of the impeller, N^* is the impeller speed, ρ_c is the density of the continuous phase, σ is the interfacial tension, b and c are correlation parameters, and φ is the dispersed phase volume fraction. Thus, the mean diameter, d , will depend on the dispersed phase fraction φ , the density of the UF solution ρ_c , the impeller speed N^* , the diameter of the impeller D_I , and the interfacial tension σ between UF solution and capsaicin.

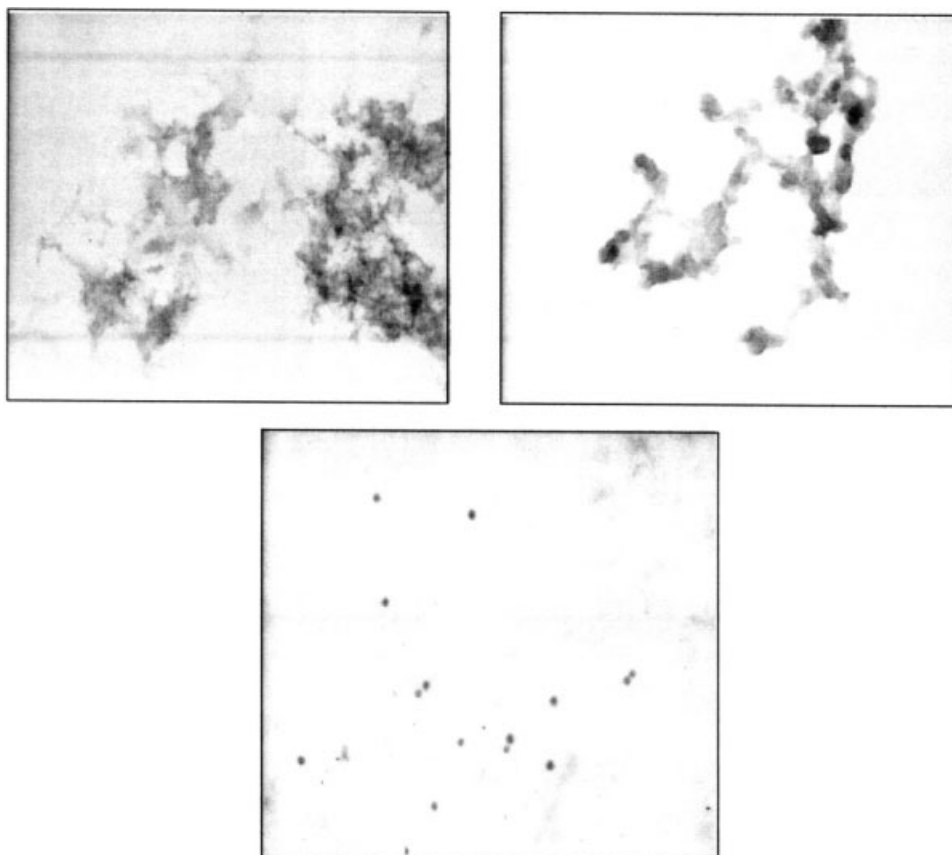


Figure 8 Morphology of MC agents ($\times 300$) (a) U/F = 1 : 1.1–1.3, no microcapsules; (b) U/F = 1 : 1.4–1.7, irregular microcapsules; (c) U/F = 1 : 1.8–2.0, globular microcapsules.

TABLE II
Influence of Acidification Time on the Morphology
of MC Agents

Acidification time/min	Phenomenon
30	Microcapsules with irregular shape
60	Microcapsules with globular shape
90	No microcapsules

Urea and formaldehyde ratio has an important role on the rate of the condensation reaction, and thus influence the particle size of MC agents. The effect of the ratio between urea and formaldehyde was investigated, and the result is presented in Table I. When the U/F ratio was 1 : 1.1–1.3, the microcapsules were decomposed and no capsules were observed by the insufficient amount of dimethylol urea. Dimethyl urea is the main substance that can be used in the condensation reaction for the development of UF resin. This is shown in Figure 8(a). But when the U/F ratio was 1 : 1.8–2.0, the agglomeration of the microcapsule became serious, and microcapsules with irregular shape can be obtained in this condition. This is shown in Figure 8(b). It has something to do with the production of trimethylol urea or tetramethyl urea, which is not

beneficial for the crosslinking reaction between urea and formaldehyde. To obtain the microcapsules with regular and globular shape, the suitable U/F ratio may be ranged from 1 : 1.4–1.7. This is shown in Figure 8(c). It shows that the MC agents have a narrow particle size distribution.

The effect of shearing force on the particle size of microcapsules is such an extent that a high shearing force yields a narrow particle size distribution range and finer average particle size. This phenomenon is directly related to the agitation rate.¹⁶ In the application of low agitation rate of stirring, the coalescence of the primary colloidal droplets continues unabatedly, leading to the formation of very large coacervate particles and, finally, to macroscopic phase separation. It can be postulated that drop breakage or smaller particle diameter d , in turbulent fields may be caused by viscous shear forces, that is the high impeller speed N^* , and the turbulent pressure fluctuations, and/or relative velocity fluctuation. This can also be deduced from Eq. (1). In our experiment, the particle size gradually decreases to a limiting value of about 40 μm as the agitation rate increases to 16,000 rpm.

Acidification time has an important influence on the synthesis of MC agents, and correlates well with

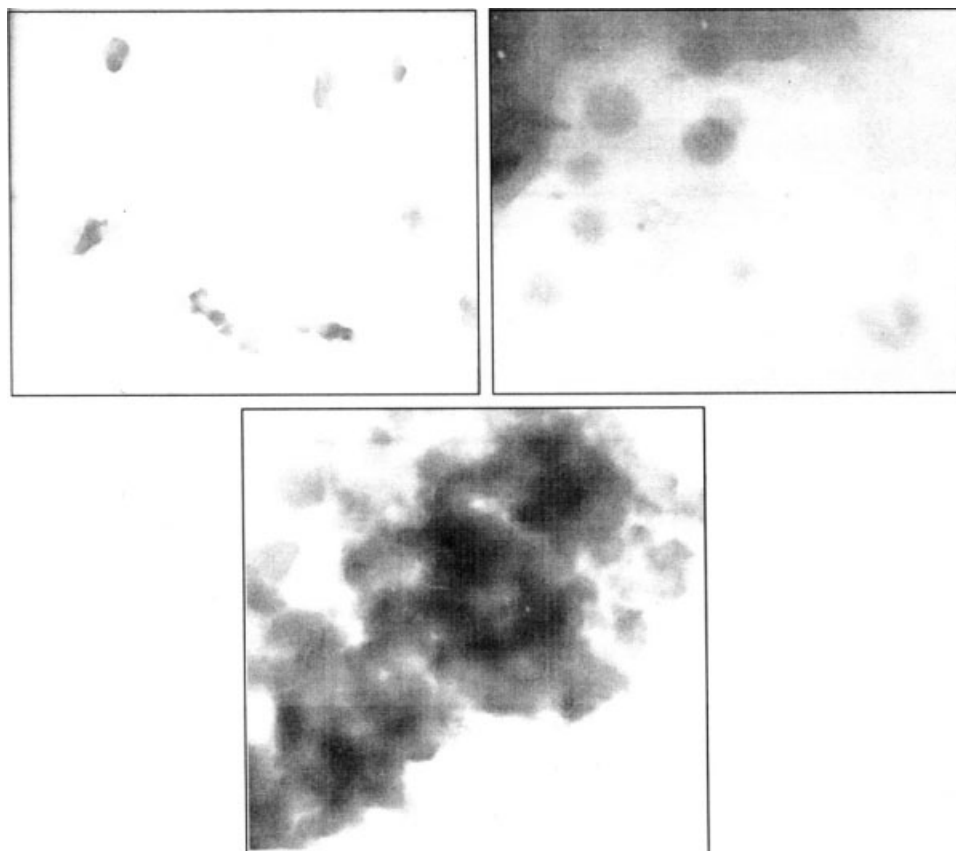


Figure 9 Morphology of MC agents ($\times 1000$) (a) acidification time 30 min, irregular microcapsules; (b) acidification time 60 min, globular microcapsules; (c) acidification time 90 min, no microcapsules.

the particle size. This tendency was associated with decreasing polymer concentration. The longer the time, the lower the viscosity is, and the smaller the particle size is.¹⁷ In general, lower viscosity liquids exhibit a smaller resistance to breakage and deformation than higher viscosity liquids when they are stirred. Consequently, they form smaller emulsion droplets compared with the high viscosity ones. The mechanism of the influence of viscosity on the particle size distribution depends on the interfacial tension σ during synthetic process. This can be seen from Eq. (1).

It is normal that, as the acidification time increases, the viscosity of the aqueous phase decreases, the distribution becomes narrower and shifts to smaller diameters.^{18–20} This can also be seen from the results shown in Table II. As shown in Figure 9(a), in the shorter acidification time (30 min), irregular microcapsules were obtained. This phenomenon is attributed to the agglomeration of the microcapsule in this condition. When the acidification time becomes longer (60 min), as shown in Figure 9(b), globe microcapsules can be obtained in this condition. This may be caused by the appropriate viscosity in this condition. However, when the acidification time was 90 min, no microcapsules can be observed. This is due to the lower viscosity of this system that is not beneficial for the development of microcapsules. This is shown in Figure 9(c).

CONCLUSIONS

A new microencapsulation was established in which small microcapsules with a UF polymeric wall could be fabricated, capsulizing the capsaicin content. The new microencapsulation is based on an *in situ* polymerization. The expected advantages of this concept of encapsulated capsaicin agent lie in its hiding pungent odor.

The morphology and size distribution of the MC agents were analyzed by FTIR spectroscopy, laser particle size analyzer, and SEM. The MC agents had a mean particle size of about 30–50 μm . In addition,

the thermal properties of the MC agents were measured by DSC and TGA. It was revealed that the melting point and thermal stability of the capsaicin were greatly improved, which was caused by the encapsulation of the crosslinked UF resin over the surface.

In conclusion, the successful synthesis of the MC agents could be related to the process conditions, such as higher shearing force (16,000 rpm agitation rate), suitable U/F ratio (1 : 1.4–1.7), appropriate acidification time (60 min), the utilization of catalyst, and the other experimental conditions, which are beneficial for the capsule wall fabrication.

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