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Factors Affecting the Characteristics of Melamine Resin Microcapsules Containing Fragrant Oils

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Abstract Microcapsules containing fragrant oils as a core material were prepared by *in situ* polymerization, using melamine-formaldehyde prepolymer as the wall material. The several parameters, such as stirring times, stirring rates, emulsifier types, emulsifier concentrations, and the viscosity of the core materials, affect the characteristics of the microcapsules. These parameters were investigated by the analyses of microcapsule size, particle size distribution, and morphology. The average microcapsule size decreased with an increase in stirring time, stirring rate, emulsifier concentration, and viscosity of the core material. It was also found that poly(vinyl alcohol) as a protective colloid could enhance the stability of the melamine-formaldehyde microcapsules.

Keywords: emulsifier, fragrant oil, *in situ* polymerization, melamine-formaldehyde, microcapsule

INTRODUCTION

Microcapsules can be defined as microscopic containers enclosing functional materials with a polymer matrix. These capsules typically range in size from several nanometers to several micrometers [1,2]. The materials that are subjected to being encapsulated are usually liquid, solid particles, or gaseous matter, which are referred to as core material, payload, or the internal phase. The material surrounding the core materials are typically synthetic or natural polymers with the ability to form a film. The coating materials must not react with the core materials used. Coating materials are referred to as wall material, membrane, or a shell [3,4]. A large number of microencapsulation techniques have been developed for the controlled release of active ingredients. Microcapsules have been widely used for various applications including carbonless copying papers, adhesives, cosmetics, insecticides, drug carriers, and by the pharmaceutical industries. Microcapsules are so widely used due to their useful functions, such as the controlled release of functional materials and their ability to protect unstable matters in a particular environment [5-8]. The recent application of microencapsulation techniques to encapsulate fragrant aromas in a polymer material for the preparation of functional fibers has gained the attention of many individuals [9].

Fragrant oils are encapsulated to improve long-term efficacy, stabilization against environmental degradation, and for easy handling through solidification of the liquid oils [10,11]. There are several chemical methods for the microencapsulation of fragrant oils, such as *in situ* polymerization, coacervation, and interfacial polymerization [5,12]. The *in situ* polymerization for the microencapsulation of fragrant oil relies on prepolymers formed in a continuous phase [11]. Urea and melamine, along with formaldehyde, have usually been used for the synthesis of a polymeric wall of the microcapsules [8,10,13]. The characteristics of microcapsules containing fragrant oils, such as morphology and particle size distribution, rely on the preparation conditions including the rate of shear, the shearing period, the kind of emulsifier used, and the viscosity of the core material [10].

In this study, melamin-formaldehyde (M-F) microcapsules containing fragrant oils were prepared by *in situ* polymerization. This work aims to investigate the characteristics of M-F microcapsules containing fragrant oils, such as their morphology, their microcapsule size, and their particle size distribution. The parameters of interest used for the preparation of M-F microcapsules include; stirring rate, stirring time, the kind of emulsifier and its concentration, the addition of a protective colloid, and the viscosity of the core material.

MATERIALS AND METHODS

Materials

Melamine and a 37% concentration of formaldehyde were used as wall materials, and obtained from Sigma-

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Aldrich (USA). Core materials used include; peppermint oil (Bolak, Korea), rosemary oil (Herbasoap, Korea), lavender oil (Herbasoap), and lemon oil (Herbasoap). The emulsifiers used, in the comparison of the morphology of the microcapsules, were Arabic gum (Daejung Chem., Korea), Tween 20 (Daejung Chem.), and sodium lauryl sulfate (SLS; Sigma-Aldrich). Poly(vinyl alcohol) (PVA; Wako Pure Chem., Japan) of DP 1,500 was used as a protective colloid. A 0.5 M NaOH (Daejung Chem.) solution and acetic acid (Daejung Chem.) were used to control the pH. All of the chemicals used in this study were reagent grade.

Preparation of Microcapsules

For the preparation of the M-F prepolymer, a mixture of melamine (0.2 M) and a 37% concentration of formaldehyde (0.6 M) in 50 mL of distilled water were adjusted to pH 8.8 ± 0.1, using a 0.5 M NaOH solution. The mixture was then stirred for 1.5 h at a temperature of 87~90°C. Simultaneously, the same amount of o/w emulsion fragrant oils were prepared in 50 mL of distilled water containing emulsifiers. The prepared emulsion and M-F prepolymer were placed in a reaction flask, and this solution was stirred with the fragrant oils for 2 h at 50°C, while the pH was gradually lowered from 8.0 to 6.5 using a 0.5 M acetic acid solution. To investigate the effect of PVA on the microencapsulation of fragrant oils, PVA was added to the preparations, followed by stirring for 2 h at 65°C with the gradual lowering of the pH from 6.5 to 5.0. After the completion of the microencapsulation, the resultant microcapsules were collected and washed with a 30% (w/v) ethanol solution and distilled water. This wash removed unreacted formaldehyde and free core materials on the surface of the microcapsules. The prepared microcapsules were then dried under a vacuum at room temperature for 24 h.

Characterization of Microcapsules

Morphologies of the M-F microcapsules were investigated by using an Olympus Model CHS optical microscope and Jeol Model JSM-5400 scanning electron microscope (SEM). For SEM analysis, the microcapsules were scattered onto a double sided tape, sputter-coated with gold, and examined with the microscope. Particle size and particle size distribution of the microcapsules were determined using an Otsuka Model ELS-8000 particle size analyzer [14]. The viscosity of fragrant oils used was determined using a Brookfield Model DV-II+Pro viscometer.

RESULTS AND DISCUSSION

Emulsifiers

Melamine-formaldehyde microcapsules were prepared by the addition of Arabic gum, SLS, and Tween 20 as emulsifiers at a concentration of 2% (w/v). During preparation the mixture was stirred at 10,000 rpm. The fragrant oil used in this experiment was peppermint oil. Fig. 1 shows SEM photographs of the microcapsules prepared using the different emulsifiers. Using Arabic gum, extreme agglomeration occurred. For SLS, the surface of the microcapsules seemed to be rough. If the microcapsules prepared with SLS were attached to fibers, the attached microcapsules may deteriorate the texture of the fiber surface. However, in the case of Tween 20, the surface of the microcapsules was smoother than the others. Kim *et al.* [15] reported that SLS was more adequate for the preparation of M-F microcapsules among the emulsifiers experimented for their particle size and distribution. In this study, the particle size of the microcapsules prepared with SLS and Tween 20 was uniform, but the surface morphologies of the microcapsules prepared with SLS and Tween 20 were rough and smooth, respectively. Thus, from this observation, it can be deduced that Tween 20 is adequate for the preparation of M-F microcapsules with regard to the morphology of the particles.

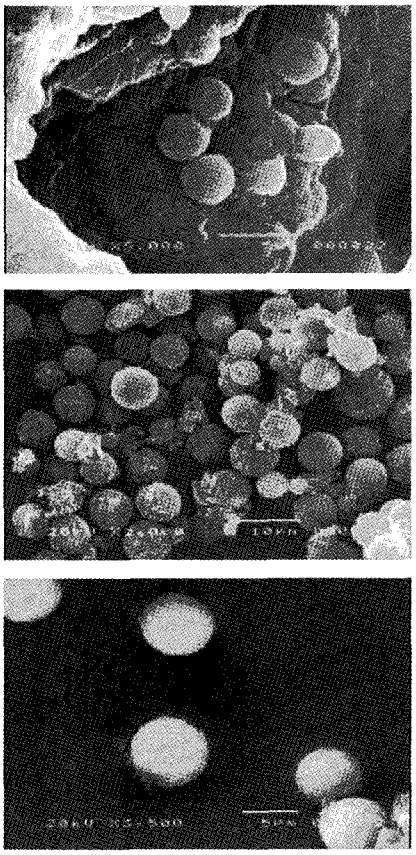

Fig. 1. Scanning electron micrographs of the microcapsules prepared using different emulsifiers. (A) Arabic gum, (B) sodium lauryl sulfate, and (C) Tween 20.

Microcapsules were prepared using Tween 20 as an emulsifier by stirring at 10,000 rpm for 20 min. During the microencapsulation process, Tween 20 was added to the reaction mixture at a concentration of 1~4% (w/v). Fig. 2A shows the mean particle sizes for the microcapsules prepared at different Tween 20 concentrations. The

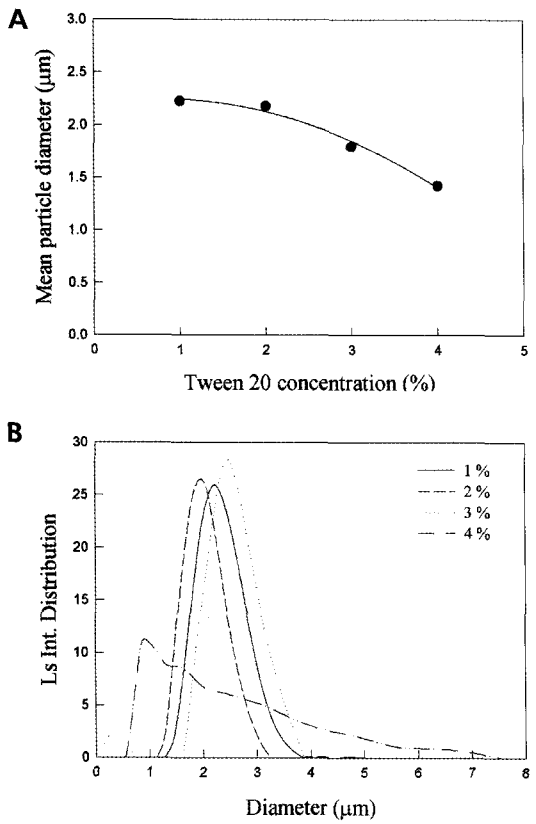

Fig. 2. The effect of Tween 20 concentrations on the mean particle diameter (A) and particle size distribution (B) of the melamine-formaldehyde microcapsules.

mean particle sizes were 2.23, 2.18, 1.79, and 1.42 μm at 1, 2, 3, and 4% of Tween 20 concentration. The mean particle size became smaller with increases in the Tween 20 concentration. Fig. 2B shows the particle size distribution of the microcapsules. The particle sizes of the microcapsules prepared using 1 and 2% of Tween 20 were distributed normally. However, two peaked regions were observed in the 3% concentration of Tween 20. The broadest distribution of the particle size was observed at a 4% concentration of Tween 20, and the narrowest at a 2% concentration of Tween 20. From these results, a 2% (w/v) concentration of Tween 20 seems to be most suitable for the preparation of the M-F microcapsules.

Addition of Poly(vinyl alcohol) As a Protective Colloid

Before the cross-linking reaction, PVA (0.002 M) was added to the reaction mixture in order to investigate the effect of a protective colloid on the morphology of the microcapsules. In this experiment, Tween 20 and peppermint oil were used as the emulsifier and core material, respectively. Fig. 3 shows the optical micrographs of the microcapsules prepared with and without PVA. As shown in this figure, the microcapsules prepared with PVA seemed to be more uniform than those prepared without PVA. In addition, when PVA was not added, significant agglomeration was observed. From this observation, it

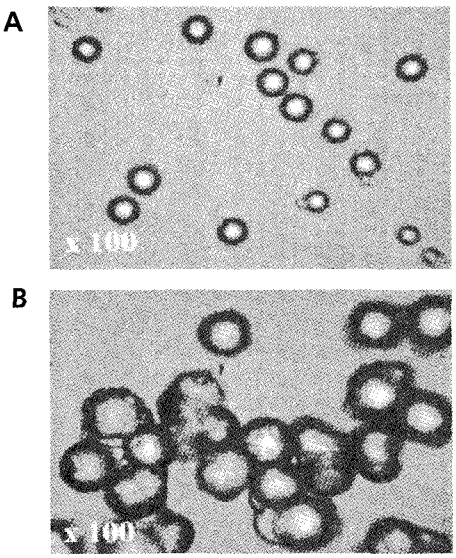

Fig. 3. Optical micrographs of microcapsules; (A) prepared with poly(vinyl alcohol) and (B) prepared without poly(vinyl alcohol).

was determined that the addition of PVA to the microencapsulation process as a protective colloid should enhance the stability of M-F resin microcapsules.

Stirring Conditions

The microcapsules were prepared using a 2% concentration of Tween 20 as an emulsifier and 0.002 M PVA as a protective colloid, while stirring at 10,000 rpm. The stirring time during the microencapsulation process varied between 2 and 30 min. As shown in Fig. 4A, the mean particle size decreased gradually with increases in the stirring time. The mean sizes of the prepared microcapsules were 4.45, 4.35, 4.01, and 2.99 μm at 2, 10, 20, and 30 min, respectively. As seen in Fig. 4B, the particle size distributions were broad at the stirring times of 2 and 10 min. At the stirring time of 30 min, the particle size distribution was similar to those at stirring time of 2 and 10 min, and a two-peaked region was observed. At a stirring time of 20 min, the particle size distribution was narrowest and exhibited a normal distribution. From these results, the optimum stirring time was found to be 20 min for the preparation of M-F microcapsules.

The stirring rates were varied from 10,000 to 17,000 rpm in order to investigate the effect of shear rate on the preparation of the microcapsules. Fig. 5A shows the mean particle sizes of the microcapsules prepared at different stirring rates. The mean particle size was reduced for stirring rate up to 13,000 rpm, but then began to increase beyond this speed. The mean particle sizes of the prepared microcapsules were 4.01, 2.16, 3.08, and 4.17 μm at 10,000, 13,000, 15,000, and 17,000 rpm, respectively. In general, as the stirring rate increased, the core material was efficiently dispersed to a continuous phase. However, the particle size increased for stirring rates above 15,000 rpm, because the high stirring rate may

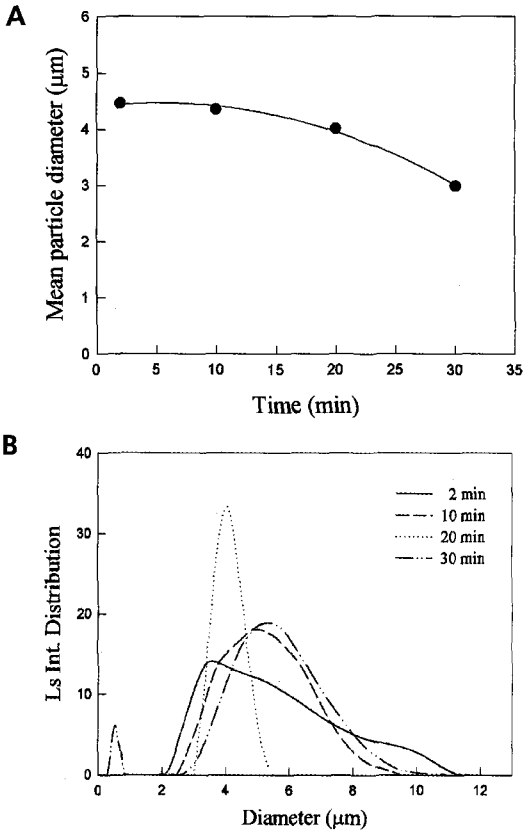

Fig. 4. The effect of stirring time on the mean particle diameter (A) and particle size distribution (B) of the melamine-formaldehyde microcapsules.

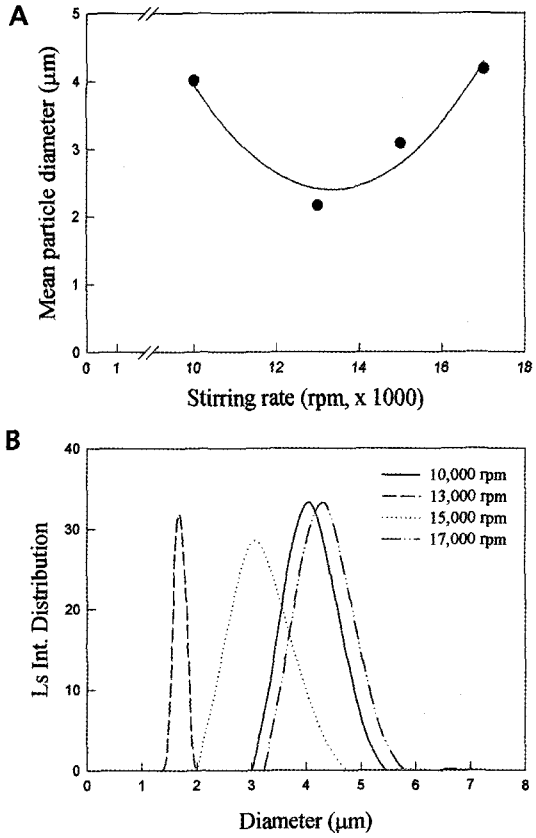

Fig. 5. The effect of stirring rate on the mean particle diameter (A) and particle size distribution (B) of the melamine-formaldehyde microcapsules.

break the generated emulsion particles and reduce the stability of the o/w emulsion. As shown in Fig. 5B, the particle size distributions exhibited a normal distribution, but the narrowest particle size distribution was observed at 13,000 rpm.

In this study, it was found that the particle size of the microcapsules generally decreased with increases in the stirring rate and stirring time. Therefore, it can be deduced that the microcapsule of a desirable particle size could be prepared through the manipulation of the stirring rate and stirring time.

Viscosity of Fragrant Oils

Several fragrant oils with different viscosities were used as core materials in order to investigate the effect of viscosity of the core material on the preparation of the microcapsules. The fragrant oils used include; peppermint, rosemary, lavender, and lemon oils. Table 1 shows the viscosities of fragrant oils used in this experiment. Among the fragrant oils tested, the viscosity of lemon oil (2.08 cP) was the lowest, and the viscosity of rosemary oil (20.8 cP) was the highest. Fig. 6 shows the mean particle sizes of the microcapsules prepared using different fragrant oils. The mean particle sizes of the microcapsules varied with the type of fragrant oil chosen, and the results were 2.16, 2.93, 2.85, and 1.22 μm for peppermint, rosemary, lavender, and lemon oils. The largest microcapsule size observed had a rosemary oil core, and the smallest one observed had a lemon oil core. Park *et al.* [10] reported that the mean particle size increased with increases in viscosity, due to the increases of interfacial tension at a high viscosity. In this study, the mean particle size of the microcapsules generally increased with increases in the viscosity of the core material used. This result suggests that particle size should rely on the viscos-

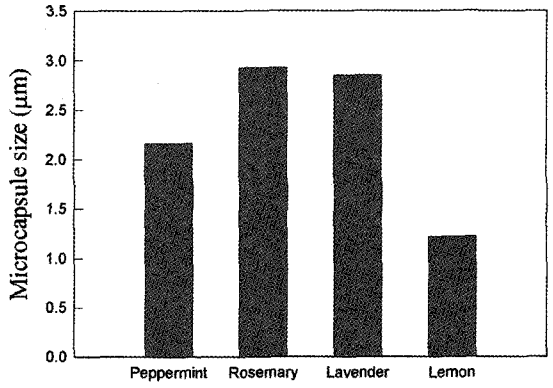

Fig. 6. The effect of the type of fragrant oils on the mean particle diameter of the melamine-formaldehyde microcapsules.

Table 1. The viscosity of fragrant oils used in this study

Fragrant oils used	Viscosity (cP)
Peppermint oil	5.04 ± 0.12
Rosemary oil	20.80 ± 0.15
Lavender oil	18.20 ± 0.20
Lemon oil	2.08 ± 0.08

ity of the fragrant oils chosen as core material. Therefore, the core material viscosity is an important parameter affecting the particle size of the M-F microcapsules.

CONCLUSIONS

In this study, M-F resin microcapsules containing fragrant oils were prepared by *in situ* polymerization, and several parameters affecting the characteristics of the microcapsules were investigated. The characteristics studied were stirring time, stirring rate, emulsifier type, emulsifier concentration, and the viscosity of the core material. Tween 20 was found to be an adequate emulsifier for the preparation of M-F microcapsules. Agglomeration of M-F microcapsules could be prevented by the addition of 0.002 M PVA before the microencapsulation process. The mean particle size generally decreased with an increase in stirring time, stirring rate, and the concentration of the emulsifier. The formation of microcapsules with good particle size distribution could be accomplished by stirring at 13,000 rpm for 20 min, using a 2% (w/v) concentration of Tween 20 as an emulsifier. In addition, the viscosity of the core material used for microencapsulation was found to be an important factor affecting the particle size of the M-F microcapsules.

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