Microencapsulation of Water-Soluble Herbicide by Interfacial Reaction. I. Characterization of Microencapsulation

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ABSTRACT: A new microencapsulation was established in which small microcapsules with a hydrophilic polymeric wall could be fabricated, capsulizing the water-soluble content. The new microencapsulation is based on an emulsion interfacial reaction technique that combines the characteristics of an interfacial reaction and conventional emulsion processes. In this technique, hydrophilic polymers [poly(vinyl alcohol) and chitosan] were used as the wall material of the microcapsules. The microencapsulation process was composed mainly of the following steps: preparation of a water/oil (w/o) emulsion 1 containing hydrophilic polymers and a water-soluble core material and w/o emulsion 2 containing a water-soluble crosslinking agent and catalyst; the formation of microcapsules by mixing emulsion 1 and emulsion 2; and washing and drying the formed microcapsules. In the new technique an insoluble polymer film was formed easily by the fast crosslinking reaction on the surface of tiny emulsified polymer solution particles in contact with the emulsified crosslinking agent solution particles under mixing with high speed agitation. Thereby, small stable microcapsules were formed. The emphasis in this study was on the establishment of the microencapsulation process by which microcapsules were formed and controlled. The microencapsulation was characterized by analysis of the size distribution of microcapsules fabricated with process conditions. The clarification of the effect of the preparation conditions was also made on the morphology and diameter of the microcapsules. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1645–1655, 2000

Key words: microencapsulation; water/oil emulsion; chitosan microcapsule; poly(vinyl alcohol) microcapsule; interfacial reactions

INTRODUCTION

In a controlled release system, the microcapsule is one of the most useful devices to deliver active materials in a more effective, longer, and safer manner. Through controlled release, existing agents with established activity prove more efficacious and newer agents whose toxicity or low stabilities have limited use may prove more suitable. Microcapsules are minute containers enclosing active materials within wall materials. The wall is often made of thin synthetic or natural polymeric membranes that can control the release of the core material. The release rate of the core materials from the microcapsules can be controlled by the chemical structure of the capsule wall, its thickness, and the particle size of the microcapsule. Microencapsulation processes can

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be largely divided into three categories: physical coating, phase separation, and interfacial reaction. The interfacial reactions utilized in microencapsulation involve interfacial polymerization, *in situ* polymerization, and the liquid curing coating process.[1–4]

In the encapsulation utilizing either interfacial polymerization or *in situ* polymerization, a monomer is the starting material and a shell wall is formed by polymerization. In contrast, a complete polymer is used as the starting material in the liquid curing coating process. The linear polymer is solubilized in a solution; but when cured, the linear polymer promptly insolubilizes and forms a film. Either water-soluble or organic solvent soluble polymers may be used. In the above process, curing of the polymer results in the formation of the shell wall of a capsule. This curing reaction proceeds quite rapidly before aggregation during wall formation and hardening. Thus, it is essential that the shape of the polymer solution containing the core material should be completely preformed prior to the addition of a curing agent. A typical process utilizing the liquid curing coating process is the orifice process. Here the encapsulation efficiency is influenced by the physical parameters associated with the orifice. The size of the resulting capsule prepared in the orifice process is relatively large.

We are interested in the efficacy of the hydrophilic polymeric wall in controlling delivery of a water-soluble herbicide through a microcapsule. Poly(vinyl alcohol) (PVA) is a typical hydrophilic polymer with a good film-forming ability. Because the crosslinking reaction of PVA with glutaraldehyde (GA) also occurs easily and quickly in aqueous solution,[5] PVA can be one of the candidates for the capsule wall. Chitosan is a low toxicity or nontoxic biodegradable polysaccharide. Because chitosan has primary amino groups, the chemical modification or crosslinking reaction is also easily conducted in an aqueous solution. Furthermore, chitosan is known to be soluble in dilute acidic solutions. Therefore, it is worth noting that utilizing chitosan as a raw material can protect the environment because of its biodegradability. This prompted us to study microencapsulation by using these materials.

For application of microcapsules to the herbicide area, a small microcapsule might be required to give a large contact area with the target plant. If capsules are not small enough, they will not adhere to the surface of the target plant quickly because of an insufficient contact area, resulting in a short dwelling time for them on the surface. This study focused on the establishment of microencapsulation by which small-sized microcapsules can be fabricated. To produce small microcapsules containing a water-soluble core material, the liquid curing coating process is suitable to employ hydrophilic polymers as a wall material. Because most of the crosslinking agents for the hydrophilic polymers are water soluble, the crosslinking reactions should be conducted in an aqueous condition during encapsulation. Therefore, this study established a new microencapsulation that can satisfy these requirements. In the new technique, small microcapsules were formed by emulsifying or dispersing the hydrophilic polymer solution containing a core material and the crosslinking agent solution in an immiscible continuous organic phase and then by a crosslinking reaction of the polymer in the interface between the phases forming the wall membrane. The emphasis in this study was put on the establishment of the microencapsulation process by which microcapsules were formed and controlled. Thus, the microencapsulation was established by using water instead of real herbicides to circumvent exposure to the danger of poisoning from the toxic compounds. The microencapsulation was characterized by analysis of the size distribution of the microcapsules fabricated with process conditions. The clarification of the effect of the preparation conditions was also made on the morphology and diameter of the microcapsules. The results obtained in this study will be utilized in future work on the preparation of microcapsules containing real water-soluble herbicides.

EXPERIMENTAL

Materials

Chitosan (extrapure grades) was purchased from Showa Chemical Inc. (Tokyo); hydrochloric acid (35% content guaranteed reagent) and GA (25% content in water, pure grade) were from Junsei Chemical Co. (Tokyo). The PVA was purchased from Aldrich Chemical Co. The average molecular weight and saponification of the PVA were 30,000 and 99%, respectively. The sorbitol-type nonionic surfactant SPAN 80 was obtained from Junsei Chemicals and H_2SO_4 was from Oriental Chemical (Seoul, Korea). *n*-Hexane and isooctane were used as the continuous phase in water/oil (w/o) emulsions of PVA and chitosan, respectively. GA was used as the crosslinking agent for PVA and chitosan, and HCl was used as a catalyst in a

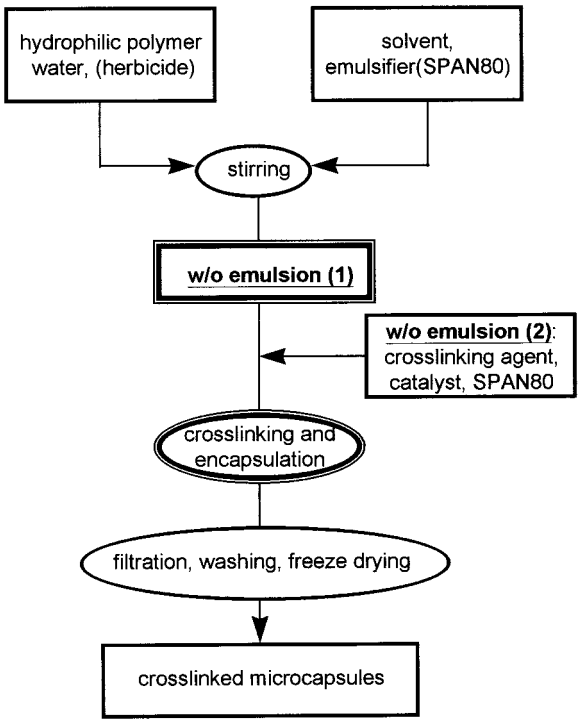

Figure 1 A schematic representation of the microencapsulation process.

crosslinking reaction between GA and PVA. H_2SO_4 was also used as another crosslinking agent for chitosan. Ultrapure deionized water was used. All chemicals were used without any further purification.

Microencapsulation

The microencapsulation process established in this study is illustrated in Figure 1. The microencapsulation process was composed mainly of three steps: preparation of water/oil (w/o) emulsion 1 containing hydrophilic polymers and a water-soluble core material and w/o emulsion 2 containing water-soluble crosslinking agent and catalyst; forming microcapsules by mixing emulsion 1 and emulsion 2; and washing and drying of the formed microcapsules. In w/o emulsion 1 the aqueous phase was composed of hydrophilic wall material (PVA or chitosan), water-soluble core material, and water while the organic phase was *n*-hexane or isooctane containing a small amount of the emulsifier SPAN 80. The aqueous phase was dispersed in the organic phase with the aid of the emulsifier under high speed agitation. In a similar manner, the aqueous phase, which consisted of crosslinking agent and catalyst dissolved in water, was dispersed in the organic phase in w/o emulsion 2. Then mixing these two emulsions at room temperature under high speed agitation for a period of time formed an insoluble polymer film by the fast crosslinking reaction between the polymer and the crosslinking agent on the surface of the emulsified polymer solution droplet in contact with the emulsified crosslinking agent solution droplet; thereby, small stable microcapsules were formed. The crosslinking reaction of PVA or chitosan with its crosslinking agent is well described elsewhere.[5–8] The reaction proceeded fast and usually reacted completely for 30 min. The fabricated microcapsules were collected by filtration and washed several times with petroleum ether and then dried by using a freeze-drying method.

The microencapsulation process condition is summarized in Table I. PVA or chitosan was used as a wall material for PVA or chitosan microcapsules, respectively, in the dispersed phase of w/o emulsion 1. In the dispersed phase of w/o emulsion 2, H_2SO_4 was used as a crosslinking agent and catalyst for the crosslinking reaction between GA and chitosan only in preparing chitosan microcapsules whereas HCl was a catalyst for the crosslinking reaction between GA and PVA in fabricating PVA microcapsules. Two stirrers were used to stir the emulsions: a mechanical stirrer (Laboratory stirrer, Talboys Eng. Corp., agitation speed 200–3500 rpm) and a homogenizer (Ultra-Turrax T25, IKA-Labortechnik, Germany, agitation speed 8000–24000 rpm). The stirring speeds in both stirrers was adjustable, and the stirring speed of the mechanical stirrer was monitored by a strobe light detector. The same agitation speeds were employed in preparing the two w/o emulsions.

Scanning Electron Microscopy

The microcapsules fabricated in this study were observed with a scanning electron microscope (SEM) (Jeol JSM-840) and a field emission SEM (FE-SEM) (Jeol model JSM-6340F). The size and shape of the microcapsules were determined from the SEM pictures. The normal SEM was used for viewing microcapsules in micrometer scale and the FE-SEM for viewing those in nanometer scale.

Capsule Size Distribution Measurements

For the measurement of the capsule size distribution, a Malvern laser diffraction particle sizer (Mastersizer X, Malvern, England) interfaced

Table I Microencapsulation Conditions for Preparation of PVA and Chitosan Microcapsules

Water/Oil Emulsion	Conditions	Amounts
1		
Continuous phase	Organic solvent	100 mL
	SPAN 80	0.5–15 mL
Dispersed phase	Aqueous polymer solution	10 mL
	Polymer concentration	0.5–10%
2		
Continuous phase	Organic solvent	100 mL
	SPAN 80	0.5–15 mL
Dispersed phase	Aqueous GA solution	0.5–5 mL
	GA content in solution	25%
	Aqueous catalyst (H_2SO_4)[a]	1–5 mL
	Catalyst (H_2SO_4) content[a]	1–10%
	HCl (35%)[b]	4 drops

[a] Only for chitosan microcapsules.
[b] Only for PVA microcapsules.

with an Olivetti computer was used. The particle size analyzer was equipped with a measurement cell. A lens capable of detecting particles in the size range of 0.1–80 μm was attached to the optical measurement unit. For the protection of the analyzer, aggravating liquids were avoided and only mild liquids, such as water and ethanol, were used for dispersing the microcapsules. However, PVA microcapsules could not be dispersed uniformly in the liquids, aggregating with each other and then resulting in a much larger measured size than the real size but the chitosan capsules were dispersed relatively well. Thus, the measurement of the PVA microcapsules failed and instead the particle size distribution was evaluated through SEM pictures.

RESULTS AND DISCUSSIONS

For the interfacial polymerization between water and organic solvents, the capsule wall is known to grow toward the phase that has a better solvent quality for the growing polymer chains.[1,2] Similarly, because the aqueous phase is a better solvent for the hydrophilic polymer in this study, the capsule wall of the w/o microcapsules grew inside toward the dispersed aqueous phase. Also, when emulsions 1 and 2 were mixed, a crosslinking reaction was very likely to take place on the surface of droplets in w/o emulsion 1 rather than in w/o emulsion 2 because moving or diffusing of polymeric chains to reaction sites was much less possible than transporting low molecular weight crosslinking agent molecules because of its high molecular weight. This indicates that the particle size distribution may be little affected by the crosslinking reaction kinetics but was affected by viscous shearing force. Therefore, viscous shear associated with the agitation speed and the concentration of the dispersing agent were found to be the crucial factors in acquiring quality microcapsules in this study.

The size of the microcapsules was dependent on the process conditions, such as the polymer concentration in the solution, the emulsifier content in the w/o emulsion, agitation speed, crosslinking agent content, the organic solvent used, and so forth. Among them, the polymer concentration and emulsifier content were the crucial factors in microencapsulation. Figure 2 presents the window on the content range of the factors for microencapsulation in which the microcapsules were fabricated. The window was established in terms of the two variables for the preparation of both PVA and chitosan microcapsules. Here the window was made in keeping the crosslinking agent content and agitation speed above their minimum values for microencapsulation, which are 0.5 vol % and 500 rpm, respectively. The microcapsules fabricated within the ranges in the window were perfectly round and covered well with polymer wall. When the emulsifier content was not high enough, the emulsifier could not effectively surround the surface of the droplets during the process and agglomeration of the microcapsule became serious. When the emulsifier content was too high in the w/o emulsion,

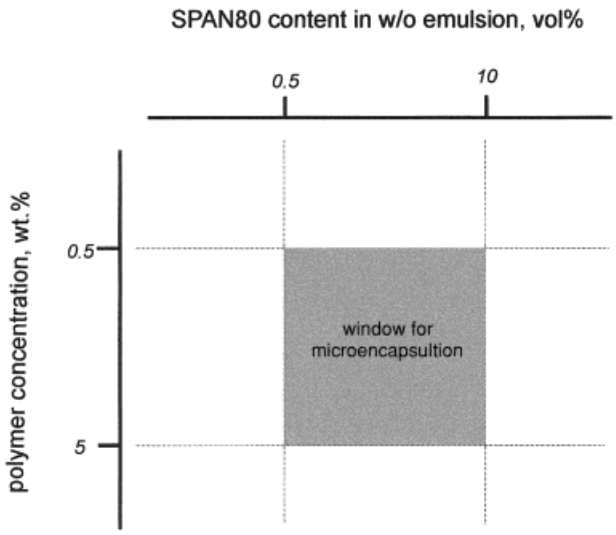

Figure 2 The window for emulsifier content and polymer concentration in microencapsulation.

excess emulsifier was introduced, slightly increasing rather than decreasing the droplet size with the increase in the content due to a too viscous medium; when the emulsifier content was too low, small droplets could not be created because of a lack of emulsifier in the emulsion. When the polymer concentration was below 0.5, the microcapsules could not be obtained because of the too thin capsule wall formed, which resulted from a too low polymer concentration. On the contrary, when the polymer content was above 5 wt %, serious cohesion occurred and dispersed microcapsules were not obtained because of viscous droplets. Therefore, the window was established as shown in Figure 2 in terms of the formation and dispersion of microcapsules.

PVA Microcapsules

The crosslinking reaction between PVA and GA catalyzed by HCl is very fast,[5] so a PVA linear polymer promptly insolubilizes and then forms a film. Thus, all of the microcapsules fabricated within the ranges in the window were perfectly spherically shaped and well covered with polymer wall. Figure 3 shows the typical effect of polymer concentration on the microcapsule size and distribution. In order to eliminate the effects of the other factor, the agitation speed and emulsifier content were kept constant at 500 rpm and 3 vol %, respectively. It reflects that the microcapsule size was strongly affected by the polymer concentration. The capsules prepared with 3 wt % polymer concentration ranged from 2 to 15 μm in size while those with 5 wt % polymer content ranged from 5 to 55 μm. The resulting capsule size was larger and the size distribution became broad at a higher polymer concentration. This tendency was associated with an increase in polymer solution viscosity with increasing polymer concentration. In general, higher viscosity liquids exhibit a greater resistance to breakage and deformation than low viscosity fluids when they are stirred. Consequently, they form larger and more stable emulsion droplets compared to the low viscosity ones. It is normal that, as the viscosity of the aqueous phase increases, the distribution becomes broader and shifts to larger diameters.[9]

Usually, at low emulsifier concentrations the interfacial tension of the disperse phase is relatively independent of the emulsifier concentration. At intermediate concentrations the interfacial tension of the disperse phase exhibits an almost linear decrease with the logarithm of the emulsifier concentration. At high concentrations

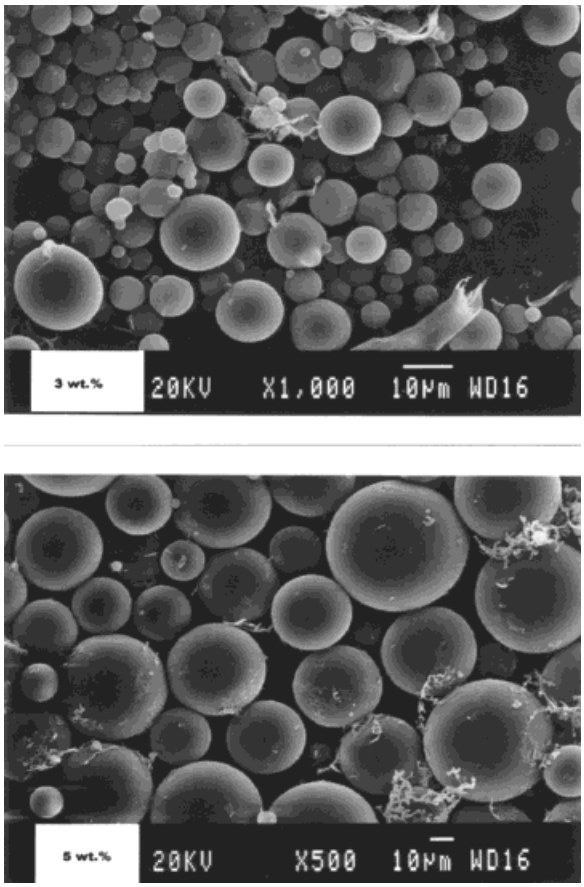

Figure 3 SEM pictures of PVA microcapsules prepared at different polymer concentrations in aqueous polymer solution. The agitation speed was 500 rpm, and the SPAN 80 content was 5%.

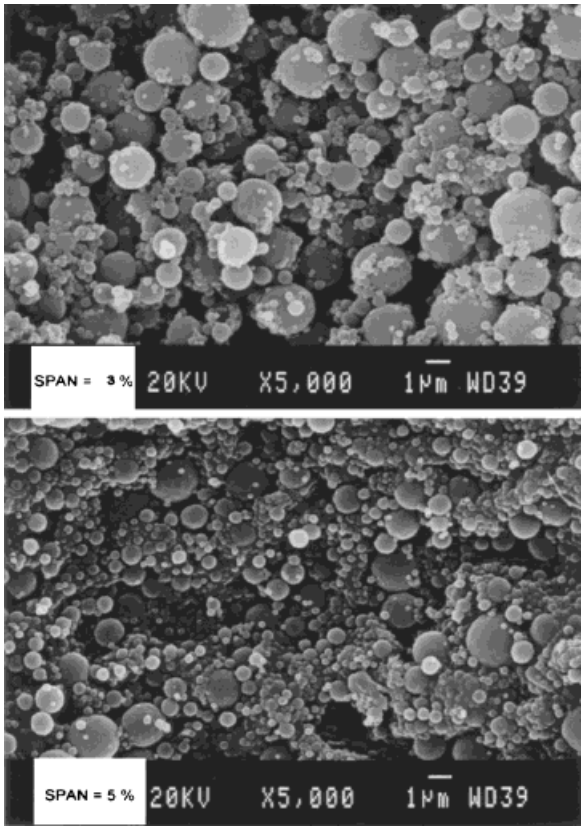

Figure 4 SEM pictures of PVA microcapsules prepared at different emulsifier contents in a w/o emulsion. The polymer concentration was 3%, and the agitation speed was 15,000 rpm.

the interfacial tension reaches a limiting value.[10] The change in interfacial tension of the polymer solution with emulsifier concentration is obviously related to the microcapsule size formed; the disperse phase (i.e., polymer solution) with less interfacial tension tends to break into smaller droplets under a certain agitation and vice versa. Thus, a higher emulsifier content would produce smaller droplets as shown in Figure 4. The average size of the microcapsules fabricated in 3% emulsifier content was about 0.6 μm while that in 5% emulsifier content was 1.5 μm. The relation between the capsule size and amount of SPAN 80 is that an increase in the concentration of the emulsifier also yields a narrow size distribution and a reduction of the average particle size.[9]

The average size of the microcapsules was reduced with increasing stirring speed as shown in Figure 5. The ultimate capsule size is determined by the size of the dispersed droplet of the first polymer. This capsule size is a direct function of the agitation rate. The effect of the agitation rate on the particle size of microcapsules prepared in the absence of an emulsifier is demonstrated to such an extent that a high agitation rate yields a narrow particle size distribution range and finer average particle size.[9,11] This phenomenon is directly related to the shearing force. It was postulated that drop breakage in turbulent fields may be caused by viscous shear forces, turbulent pressure fluctuations, and/or relative velocity fluctuation. However, at agitation rates above 8000 rpm, no significant variation of the drop size distribution is observed with the agitation rate as shown in Figure 6 where the droplet average diameter is plotted with respect to the agitation rate. It is evident that as the agitation rate in-

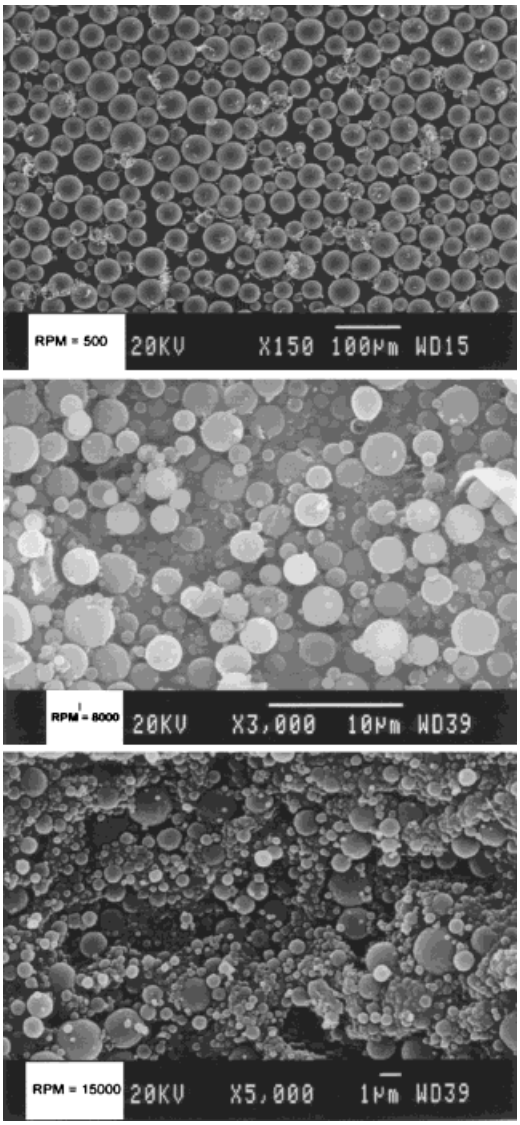

Figure 5 SEM pictures of PVA microcapsules prepared at different agitation speeds. The polymer concentration was 3%, and the emulsifier content was 5%.

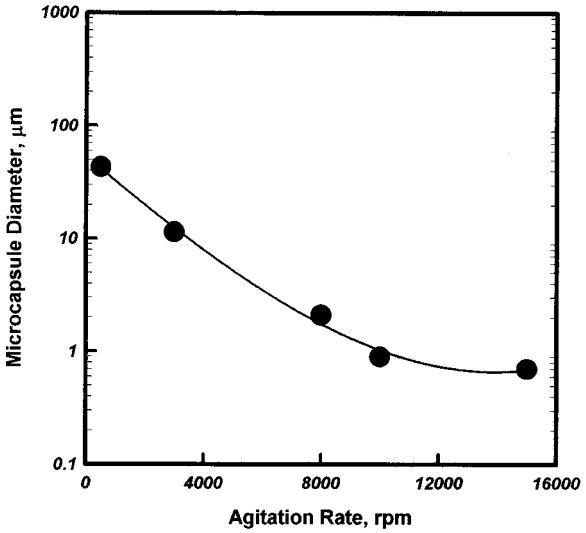

Figure 6 A plot of the average PVA microcapsule diameter against agitation rate. The polymer concentration was 3%, and the emulsifier content was 5%.

creases, the microcapsule size sharply decreases to a limiting value of about 0.6 μm.

When the PVA concentration was 1 wt %, microcapsules could hardly be formed at a low agitation rate of 500 rpm, and mainly the polymer debris and broken capsule walls were found from the SEM pictures of the prepared microcapsules. This might be explained in terms of a imbalance between the capsule size and thickness of the prepared capsule wall. The capsule wall fabricated at lower polymer concentration could be thinner[8] while capsules prepared at low agitation speed could be large. Therefore, the microcapsules prepared at low polymer concentration and low agitation speed were too thin for their wall thickness so that they could not maintain their capsule shape and were finally broken by shear force during the encapsulation process because of poor mechanical strength. However, when the agitation rate was sufficiently high, the capsules could be formed even at 1 wt % of the PVA concentration as can be seen in Figure 7. This is because the microcapsules have a small diameter and thin capsule wall so that the thin capsule wall formed can be balanced with the small size of the microcapsule. Thus, very small microcapsules (40–80 nm in diameter) could be obtained in this process condition.

The effect of crosslinking agent content was also investigated and the result is presented in Figure 8. As discussed previously, the ultimate capsule size is determined by the size of the dispersed droplet of the first polymer solution because drop breakage in turbulent fields may be caused by viscous shear forces induced by agitation. Thus, it is essential that the shape of the polymer solution containing the core material be completely preformed prior to the addition of a curing agent. As a result, the crosslinking agent content could little affect the particle size and distribution of the microcapsule, even if it was higher than the critical content found (0.5 vol %). Below 0.5 vol % the wall could not be formed because of an insufficient crosslinking reaction due to a lack of crosslinking agent in the system.

Fabrication of Chitosan Microcapsules

Figure 9 presents the SEM pictures of microcapsules prepared by the crosslinking reaction between chitosan and GA at different polymer concentrations and emulsifier contents. The result-

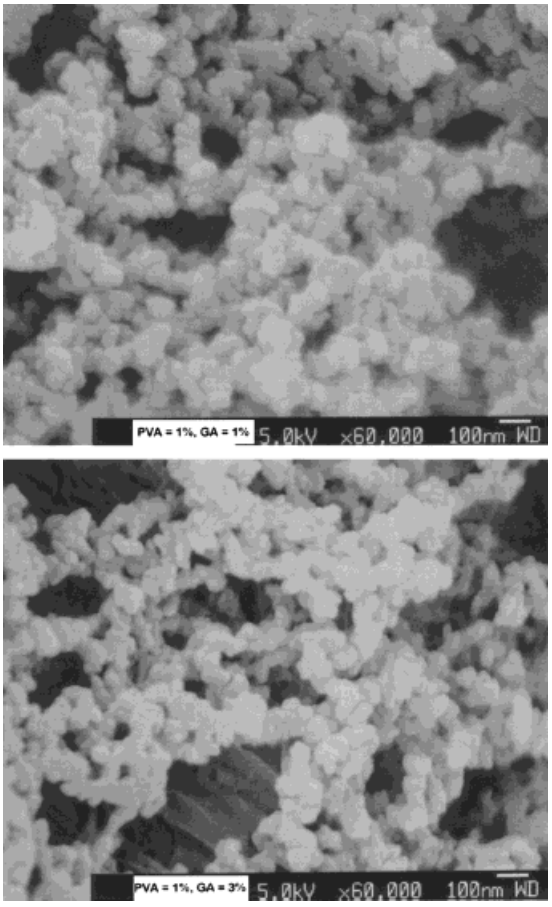

Figure 7 FE-SEM pictures of PVA microcapsules fabricated at different glutaraldehyde contents in w/o emulsion 2. The polymer concentration was 1%, the agitation speed was 8000 rpm, and the emulsifier content was 5%.

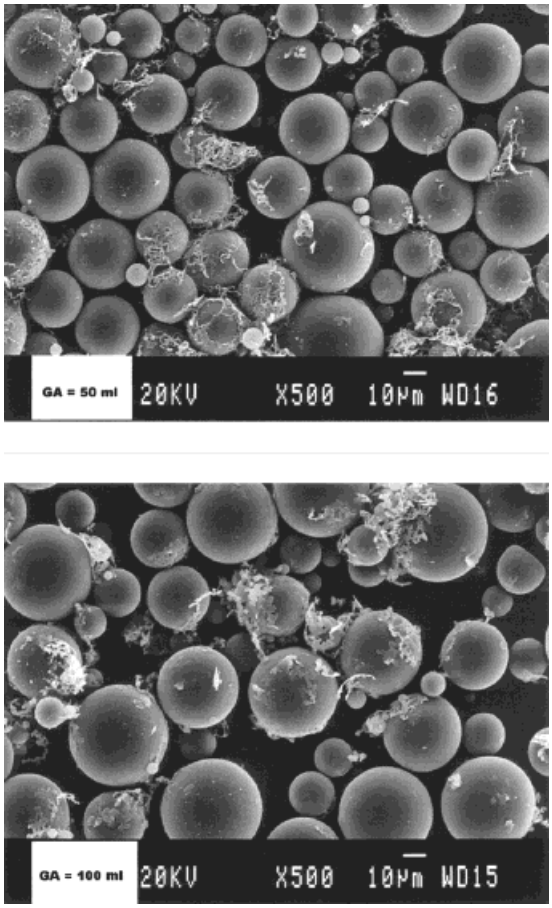

Figure 8 FE-SEM pictures of PVA microcapsules fabricated at different glutaraldehyde contents in w/o emulsion 2. The polymer concentration was 1%, and the agitation speed was 8000 rpm.

ing microcapsules have a deformed-sphere shape. The reason for that is not clear, but it may be related to the relatively slow reaction between the chitosan and the crosslinking agent during the encapsulation process. The effects of polymer concentration and emulsifier content are the same as in the microencapsulation of PVA: the higher the emulsifier content is, the smaller the microcapsules produced [Fig. 9(a, b)]; the higher the polymer concentration is, the larger the microcapsules are [Fig. 9(b, c)]. The average capsule sizes in Figure 9(a–c) are about 7.5, 3, and 7 μm, respectively. Figure 10 exhibits the particle size distributions of the microcapsules shown in Figure 9. The size distributions were directly measured by the laser diffraction particle sizes. It can be seen that the measurement results are in good agreement with the size distributions deduced from the SEM pictures in Figure 9.

Mochizuki et al.[6] reported that the polybasic acid H_2SO_4 can be used as a crosslinking agent for the ionic crosslinking of chitosan by neutralization between the acid and amine in chitosan. Usually, ionic crosslinking reactions are very fast, which is very important for the formation of stable microcapsules. In addition, the acid can act as a catalyst for the crosslinking reaction between GA and hydroxyl groups.[5] Therefore, when H_2SO_4 was added to w/o emulsion 2, microcapsules were formed by possibly three reactions: the neutralization between the acid and the amines in chitosan, the crosslinking reac-

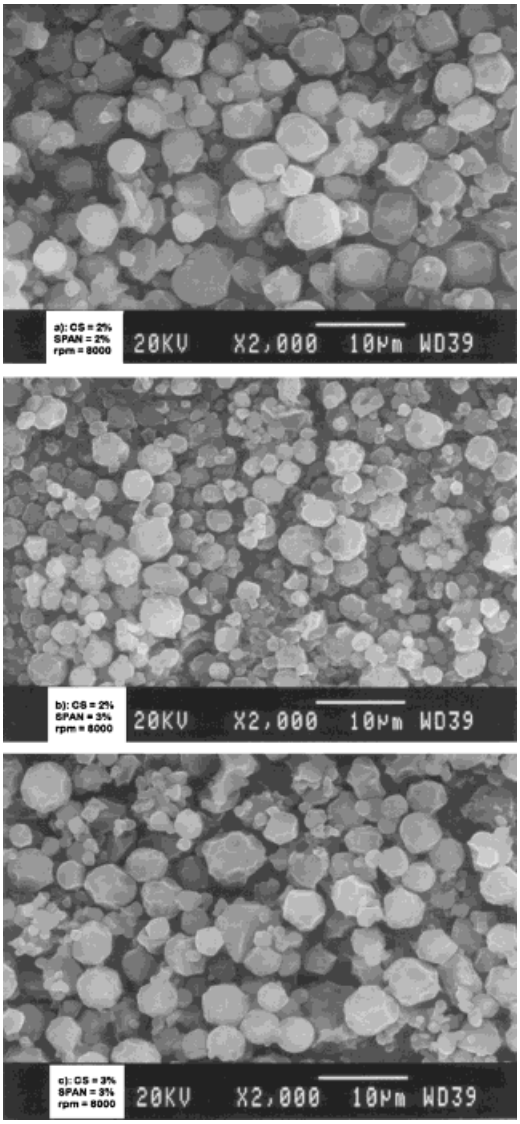

Figure 9 FE-SEM pictures of chitosan microcapsules fabricated at different polymer concentrations and emulsifier contents. The agitation speed was 8000 rpm. (a) The polymer concentration was 2%, and the emulsifier content was 2%; (b) the polymer concentration was 2%, and the emulsifier content was 3%; (c) the polymer concentration was 3%, and the emulsifier content was 3%.

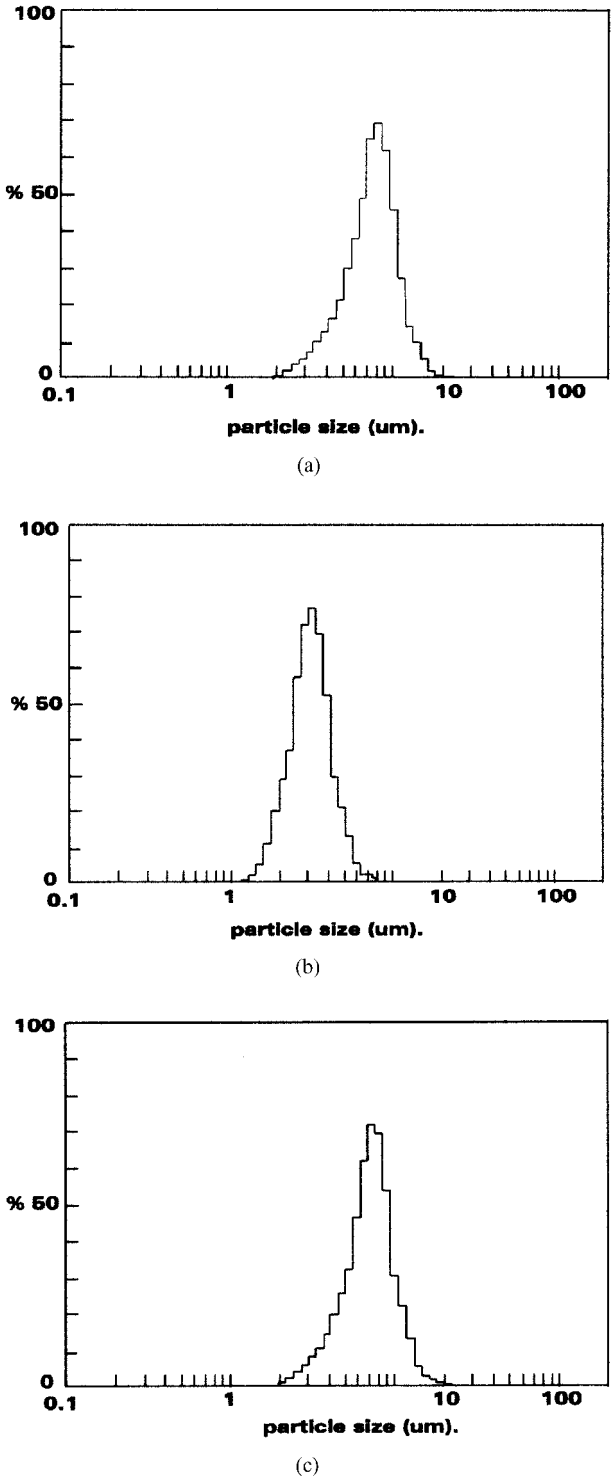

Figure 10 The particle size distribution of chitosan microcapsules in Figure 9. The agitation speed was 8000 rpm. (a) The polymer concentration was 2%, and the emulsifier content was 2%; (b) the polymer concentration was 2%, and the emulsifier content was 3%; (c) the polymer concentration was 3%, and the emulsifier content was 3%.

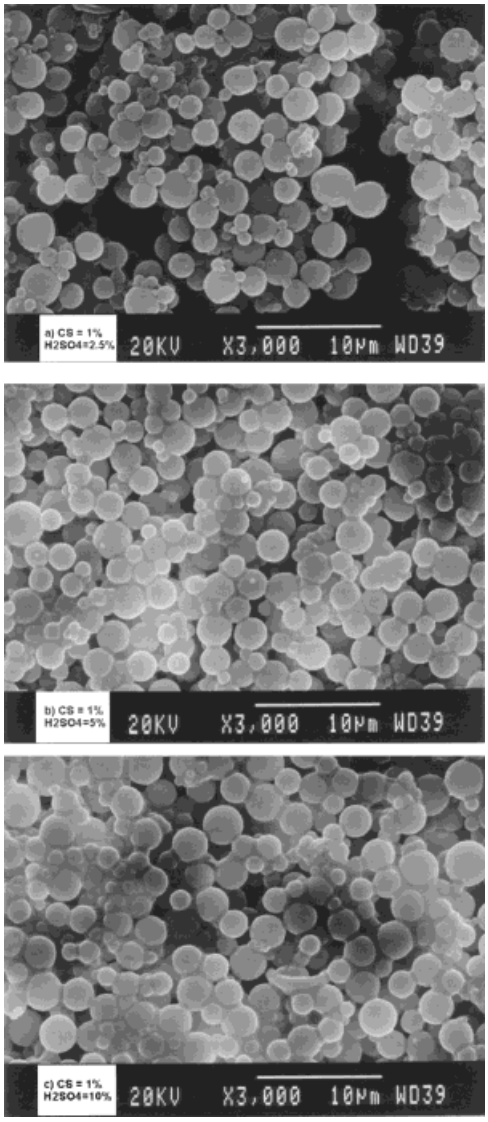

Figure 11 SEM pictures of chitosan microcapsules fabricated at different H_2SO_4 contents in w/o emulsion 2. The polymer concentration was 1%, the aqueous H_2SO_4 solution amount (2) was 2 mL, the glutaraldehyde amount was 5 mL, the agitation speed was 8000 rpm, and the emulsifier content was 3%.

tion between GA and the amines, and the crosslinking reaction between GA and the hydroxyl groups in the chitosan. Thus, the crosslinking reaction proceeds faster and to a larger extent. This could be confirmed by the experiment; the formation of microcapsules was observed to be more accelerated by the addition of H_2SO_4 to w/o emulsion 2 and the formed microcapsules were more stable in the emulsion solution. Figure 11 presents SEM pictures of the microcapsules prepared by adding different contents of H_2SO_4 aqueous solutions into w/o emulsion 2. At an H_2SO_4 content higher than 2.5% in the

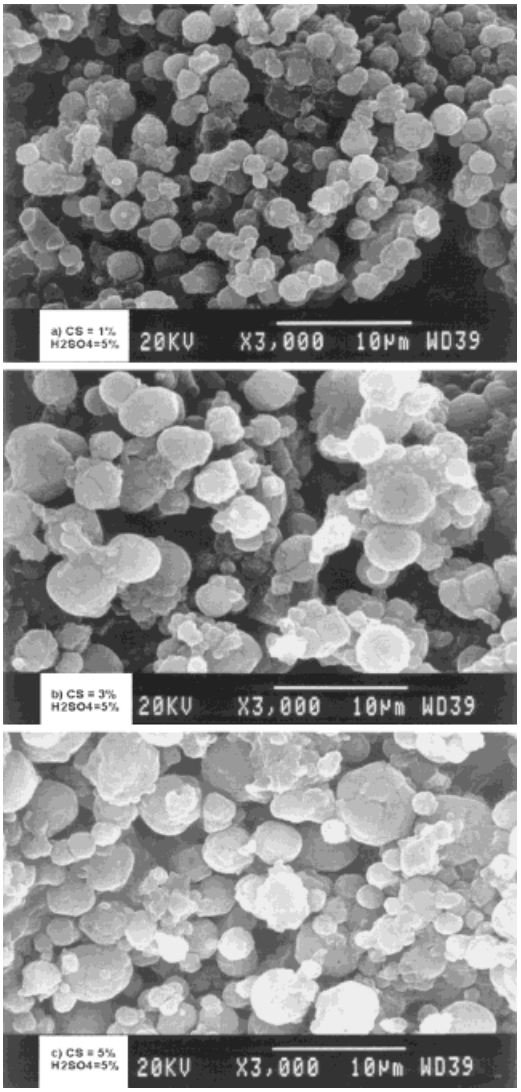

Figure 12 SEM pictures of chitosan microcapsules fabricated at different polymer concentrations by using H_2SO_4 crosslinking agent. The H_2SO_4 content in the aqueous H_2SO_4 solution was 5%. The aqueous H_2SO_4 solution amount in the w/o emulsion 2 was 5 mL, the glutaraldehyde amount in w/o emulsion 2 was 0 mL, the agitation speed was 8000 rpm, and the emulsifier content was 3%.

aqueous solution, the resulting microcapsules all have a perfect spherical shape like the PVA microcapsules. However, below 2.5% H_2SO_4 content, the prepared capsules were a deformed-round shape, similarly to those shown in Figure 9. In Figure 11 the capsule size seems to be independent of the H_2SO_4 content. This reconfirms that the ultimate capsule size is determined by the size of the dispersed droplet of the first polymer, which is associated with the viscous shear force applied to the system and is not affected by the curing kinetics. It is observed from Figure 11 that the diameter of the resulting capsules ranges from 0.8 to 3 μm and the average diameter is 2 μm, which shows a narrow distribution. On the other hand, when H_2SO_4 was used alone as the crosslinking agent in w/o emulsion 2, the aggregation between droplets took place during encapsulation so that stable microcapsules could not be obtained as can be seen in Figure 12. Cracks and loose structure on the capsule surface

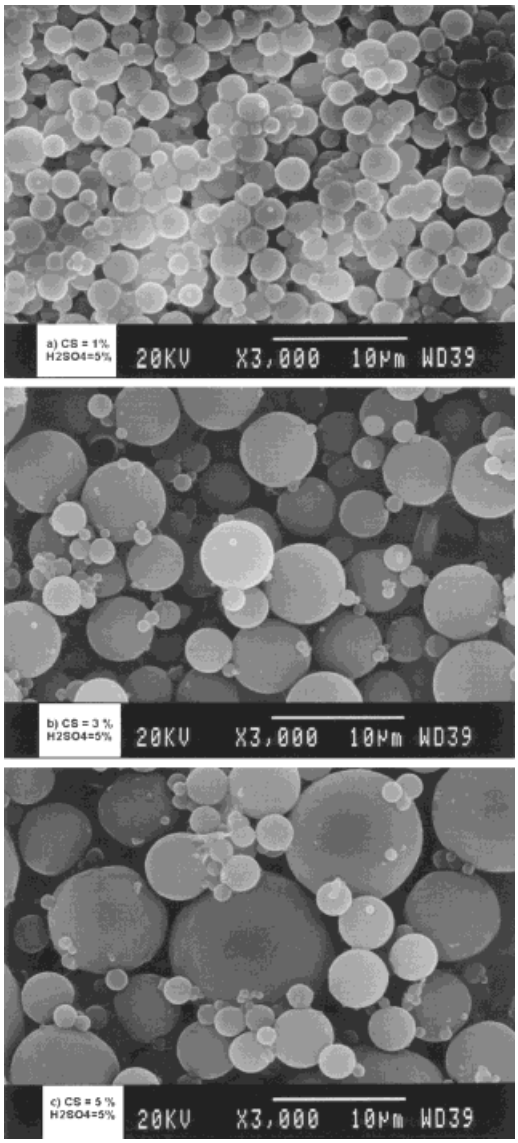

Figure 13 SEM pictures of chitosan microcapsules fabricated at different polymer concentrations under the H_2SO_4/glutaraldehyde crosslinking agent system. The H_2SO_4 content in the aqueous H_2SO_4 solution was 5%, the aqueous H_2SO_4 solution amount in w/o emulsion 2 was 2 mL, the glutaraldehyde amount in w/o emulsion 2 was 5 mL, the agitation speed was 8000 rpm, and the emulsifier content was 3%.

were also found. Usually, a polymer crosslinked by ionic crosslinking or ionic complexation under aqueous circumstances is too swollen by water because of its high affinity toward water. So the surface of the resulting microcapsule might have some adhesive strength to aggregate with each other during the microencapsulation process. Also, the drastic volume contraction occurring in freeze-drying would develop a stress across the wall thickness and then cause cracks in the wall. Figure 13 shows the SEM pictures of microcapsules fabricated at different chitosan concentrations in the presence of H_2SO_4/GA in w/o emulsion 2. All of the capsules have a perfectly spherical shape and smooth surface, regardless of the polymer concentration. The capsules exhibit a tendency to have a larger diameter and broader size distribution at higher polymer concentration as found in the previous cases. As a result, we concluded from our observations that the efficient crosslinking agent for chitosan is the H_2SO_4/GA mixed system.

CONCLUSIONS

In this study, several significant conclusions can be drawn from the results obtained.

1. A new microencapsulation was developed by which small microcapsules with hydrophilic polymeric walls can be fabricated. The microencapsulation process was composed mainly of the following steps: preparation of w/o emulsion 1 containing hydrophilic polymers and a water-soluble core material and w/o emulsion 2 containing a water-soluble crosslinking agent and catalyst; forming microcapsules by mixing the emulsions; and washing and drying of the formed microcapsules.
2. PVA and chitosan were selected for the capsule wall materials because a fast crosslinking reaction could be available for these polymers and the reaction could occur even in aqueous conditions.
3. The size distribution of microcapsules was not affected by the crosslinking reaction kinetics but was affected by viscose shearing force. Thus, the ultimate capsule size is a direct function of the polymer concentration, emulsifier content, and agitation speed.
4. The crosslinking reaction took place on the surface of the droplets in w/o emulsion 1 rather than in w/o emulsion 2 because moving or diffusing of polymeric chains to reaction sites is much less possible than transporting of low molecular weight crosslinking agent molecules because of its high molecular weight.
5. PVA microcapsules of nanometer scale could be prepared at low polymer concentration and high agitation speed because of a very fast crosslinking reaction and its good film-forming property.
6. Perfectly spherical shaped chitosan microcapsules could be obtained by using the H_2SO_4/GA mixed system as crosslinking agent in w/o emulsion 2. The diameter of the resulting capsules ranged from 0.8 to 3 μm and the average diameter was 2 μm, showing a narrow size distribution.

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