Microencapsulation of Water-Soluble Herbicide by Interfacial Reaction. II. Release Properties of Microcapsules

C. K. YEOM, Y. H. KIM, J. M. LEE

Chemical Process and Engineering Center, Applied and Engineering Chemistry Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejon 305-606, South Korea

Received 12 October 2000; accepted 13 August 2001

ABSTRACT: Chitosan microcapsules containing the water-soluble herbicide 3-hydroxy-5-methylisoxazole were fabricated at different fabrication conditions by a new microencapsulation process established in the previous work. Selecting chitosan as a capsule wall could be justified because chitosan not only has a biodegradable characteristic but also enhances the fertility of soil after degradation in the ground. The microcapsules prepared at an agitation speed of higher than 12,000 rpm were smaller than 5 μm in diameter, and the release of the active material from the capsules into pure water was sustained for 80–160 h, depending on the agitation speed used in microencapsulation. The effects of fabrication variables were discussed on the capsule size and release properties of the fabricated microcapsules. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1025–1034, 2002; DOI 10.1002/app.10383

Key words: microencapsulation; water/oil emulsion; chitosan microcapsule; water-soluble herbicide; hymexazol; interfacial reactions

INTRODUCTION

There is a growing interest in the application of a controlled-release system, especially microcapsules to deliver active materials at a controlled rate.[1–4] The microcapsule can be one of the most useful devices to release herbicides in a more effective, longer, and safer manner. Controlled release of herbicides from microcapsules can prevent wasting the active materials and contaminating the environment by their excess dosage.

For application of microcapsules to the herbicide area,[3–5] the small size of microcapsules might be required to give a large contact area with target plants. If capsules are not small enough in size, they will not adhere fast to the surface of the target plant because of insufficient contact area, resulting in their short dwell time on the surface. In addition, the microcapsule should have a long durability in releasing the active material. In the previous work,[6] a new microencapsulation process was established by which small microcapsules with a hydrophilic polymeric wall could be fabricated. The new microencapsulation technique could satisfy these requirements mentioned above in preparing microcapsules. The microencapsulation process was composed mainly of the following steps: (i) preparation of water/oil emulsion 1, containing hydrophilic polymers and a water-soluble core material, and water/oil emulsion 2, containing water-soluble crosslinking agent and catalyst; (ii) forming microcapsules by mixing the emulsions; and (iii) washing and drying of the formed microcapsules. In the new technique, an insoluble hydrophilic polymer film was formed easily by a fast crosslinking reaction on the surface of tiny emulsified

Correspondence to: C. K. Yeom (ckyeom@pado.krict.re.kr).

Journal of Applied Polymer Science, Vol. 84, 1025–1034 (2002)

polymer solution particles in contact with the emulsified crosslinking agent solution particles in mixing under high-speed agitation and, thereby, stable microcapsules of small size were formed. Poly(vinyl alcohol) and chitosan were selected for materials of the capsule wall, and a perfect spherical shape of chitosan microcapsule could be obtained by using the H_2SO_4/glutaraldehyde dual crosslinking agent system as crosslinking agent, ranging from 0.8 to 3 μm in diameter and showing a narrow size distribution.

Chitosan is a typical hydrophilic polymer and a low or nontoxic biodegradable polysaccharide having a good film-forming ability. Because chitosan has primary amino groups, chemical modification or crosslinking reaction is easily and quickly conducted in aqueous solution. Furthermore, chitosan is known to be soluble in dilute acidic solutions. In addition, selecting chitosan as a capsule wall could be justified because chitosan not only has a biodegradable characteristic but also enhances the fertility of soil after degradation in the ground. This has prompted us to study microencapsulation by using the materials.

The purpose of this study is to fabricate chitosan microcapsules containing a water-soluble herbicide, by utilizing the results obtained from the new microencapsulation technique in the previous work, and to investigate the release properties of the prepared microcapsules. An environmentally friendly microcapsule can be prepared by using chitosan. 3-Hydroxy-5-methylisoxazole (Hymexazol), which is known as an agricultural fungicide and plant growth regulator, was chosen as the model of water-soluble herbicide. Chitosan microcapsules were prepared at different process conditions by the new technique, and the release tests with the microcapsules were carried out. The process condition effects were discussed on the capsule size and release properties of the fabricated microcapsules. This study focuses on the microencapsulation of an herbicide using the biodegradable polymer chitosan as a wall material and the investigation of the basic release property of the herbicide from the fabricated microcapsule.

EXPERIMENTAL

Materials

Chitosan (extrapure grades) was purchased from Showa Chemical Inc. (Tokyo, Japan), hydrochloric acid (35% content guaranteed reagent) and glutaraldehyde (GA; 25% content in water, pure grade) from Junsei Chemical Co. (Tokyo, Japan). SPAN 80 (nonionic surfactant of the sorbitol type) was obtained from Junsei Chemical and H_2SO_4 from Oriental Chemical (Seoul, Korea). Isooctane was used as the continuous phase in water/oil emulsions of chitosan. GA was used as a crosslinking agent of chitosan, and H_2SO_4 was also used as another crosslinking agent of chitosan as well as a catalyst for the crosslinking reaction between glutaraldehyde and chitosan. The water-soluble herbicide 3-hydroxy-5-methylisoxazole was generously provided by Dongyang Chemical (Seoul, Korea). Ultrapure deionized water was used. All chemicals were used without any further purification.

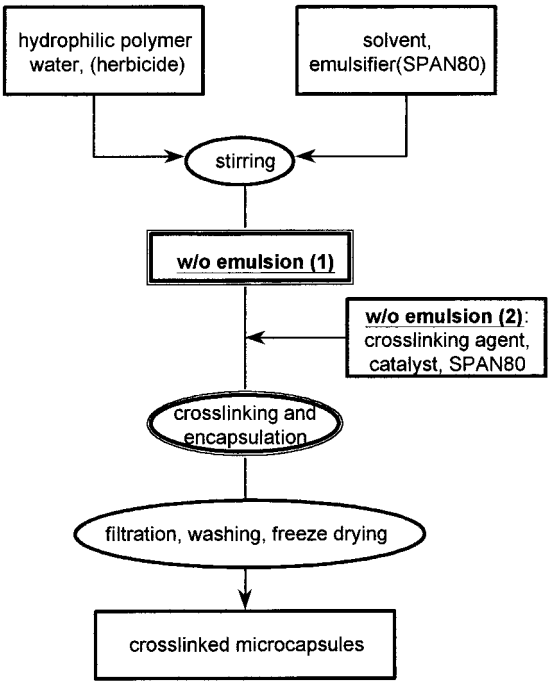

Figure 1 Schematic representation of microencapsulation process; w/o = water/oil.

Microencapsulation

The microencapsulation process used in this study is well described elsewhere[6] and is illustrated in Figure 1. The microencapsulation process was composed mainly of three steps: (i) preparation of water/oil emulsion 1 containing a hydrophilic polymer and a water-soluble herbicide, Hymexazol, and water/oil emulsion 2 containing a water-soluble crosslinking agent and catalyst; (ii) forming microcapsules by mixing emulsion 1 and

Table I Microencapsulation Conditions for the Preparation of Chitosan Microcapsules

Water/Oil Emulsion	Condition	Amount
Water/oil emulsion 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%
Water/oil emulsion 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%
	H_2SO_4	1–5 mL
	H_2SO_4 content	1–10%

emulsion 2; and (iii) washing and drying of the formed microcapsules. In water/oil emulsion 1, the aqueous phase was composed of the hydrophilic polymer (chitosan), the water-soluble core material, and water, whereas the organic phase was an isooctane containing a small amount of an 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 water/oil emulsion 2. When these two emulsions were mixing under high-speed agitation, an insoluble polymer film was formed by the fast crosslinking reaction between the polymer and the crosslinking agent on the surface of the emulsified polymer solution droplets in contact with the emulsified crosslinking agent solution droplets and, thereby, stable microcapsules of small size were formed. The crosslinking reaction of chitosan with its crosslinking agents was well described elsewhere.[6–8] The reaction proceeded fast and usually allowed to react completely for 30 min. The fabricated microcapsules were collected by centrifugal separation, washed several times with petroleum ether, filtrated, and then dried by using a freeze-drying method.

The microencapsulation process conditions are summarized in Table I. In stirring the emulsions, two stirrers were used, that is, a mechanical stirrer (laboratory stirrer, agitation speed, 200–3500 rpm; Talboys Engineering Corp., NJ) and a homogenizer (Ultra-Turrax T25, agitation speed, 8000–24,000 rpm IKA Labortechnik, Germany). The stirring speeds in both the stirrers could be adjusted and the stirring speed of the mechanical stirrer, in particular, was monitored by a strobe light detector. The same agitation speeds were employed in preparing the two water/oil emulsions.

Scanning Electron Microscopy (SEM)

The microcapsules fabricated in this study were observed by a scanning electron microscope (SEM) (JEOL Model JSM-840; JEOL, Peabody, MA) and a field-emission SEM (FE-SEM) (JEOL Model JSM-6340F). The size and shape of microcapsules were determined from SEM photomicrographs. The normal SEM was used for viewing microcapsules in micrometer scale and the FE-SEM for viewing those in nanometer scale.

Release Test

The release tests of the microcapsules were performed at 30°C by placing 0.2 g of the capsules in a bath filled with 1 L of pure water. This water volume is substantially in excess of that required to dissolve all of the herbicide. The bath is depicted in Figure 2. Pure water was used as dissolution medium. Samples at predetermined intervals were taken from the bath for evaluation of the content of the herbicide released into the pure water with time. To remove any microcapsules involved in each sample, the sample underwent centrifuging separation before measuring its content. Hymexazol was monitored in the sample by absorbance at 200 nm (UV spectrophotometer, UV-160A; Shimadzu, Tokyo, Japan). The bath has a jacket for circulating water to thermostat

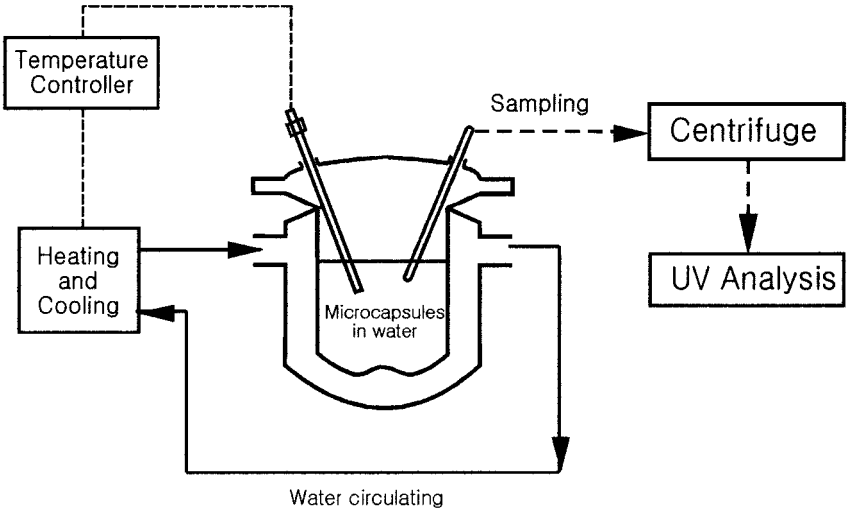

Figure 2 Schematic representation of apparatus for the release test of microcapsules.

the dissolution medium to the desired temperature of 30°C.

RESULTS AND DISCUSSION

Microcapsules Fabricated with Encapsulation Variables

In the previous work, the dual crosslinking agent system GA/H_2SO_4 had been developed for the crosslinking reaction of chitosan.[6] Two reactions between chitosan and the dual crosslinking agent system took place: the ionic crosslinking reaction[7] between the acid and the amines in chitosan; the covalent crosslinking reaction[8] between GA and the hydroxyl groups in chitosan. The crosslinking reactions proceeded very fast and effectively on the surface of small polymer solution droplets formed under a certain agitation, so the chitosan polymer promptly insolubilized and then formed a capsule wall. Therefore very stable and perfectly spherically shaped microcapsules could be obtained. Generally, the hydrophilic capsule wall of water/oil microcapsules grew inside toward the dispersed aqueous phase that is a better solvent than the continuous organic phase for the hydrophilic polymer in this study, as in the interfacial polymerization technique in which the capsule wall grows toward the phase that has a better solvent quality for the growing polymer chains.[1,2] It was also observed that the crosslinking reaction takes place and the capsule wall is then formed on the surface of droplets in water/oil emulsion 1, rather than in water/oil emulsion 2, in the new microencapsulation process because moving or diffusing of polymeric chains with high molecular weight to reaction sites is much less possible than transporting of crosslinking agent molecules with low molecular weight. From these observations, it could be summarized that microcapsule size is only slightly affected by crosslinking reaction kinetics but is dependent mainly on viscous shear in the water/oil emulsion. Therefore, important fabrication variables associated with viscous shear could be polymer concentration in dispersed phase, emulsifier concentration in water/oil emulsion, and agitation speed, which were found to be the crucial factors in acquiring quality microcapsules in this study.

Table I summarizes the microencapsulation process conditions in which the microcapsules were able to be fabricated. The microcapsules fabricated within the range of the process conditions were perfectly spherical in shape, well covered with the polymer wall. When the emulsifier content was too high in forming an emulsion, excess emulsifier was introduced, slightly increasing rather than decreasing the droplet size with increasing the content resulting from the too-viscous medium. When the emulsifier content was too low, small-size droplets could not be created because of lack of emulsifier in the emulsion and the agglomeration of microcapsules severely increased. When the polymer concentration in the aqueous phase was below 0.5 wt %, the microcapsules could not be obtained because of the too-thin capsule wall, formed as a result of the too-low polymer concentration. On the contrary, when the

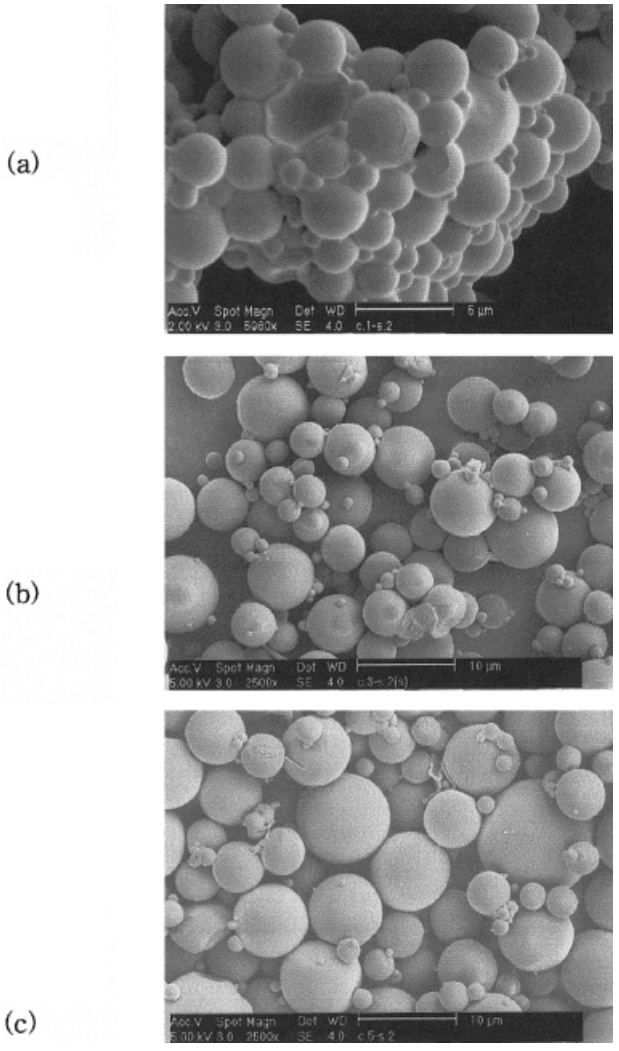

Figure 3 SEM photomicrographs of chitosan microcapsules prepared at different polymer concentrations in aqueous polymer solution (agitation speed = 8000 rpm, SPAN 80 content = 2 wt %): polymer solution (a) 1 wt %; (b) 3 wt %; (c) 5 wt %.

polymer content was above 5 wt %, severe cohesion occurred and disperse microcapsules were not obtained because of droplet viscosity. The crosslinking agent content and agitation speed had to be kept above their minimum values for microencapsulation, which were 0.5 vol % and 500 rpm, respectively.

Figure 3 shows the typical effect of polymer concentration in the aqueous phase on the microcapsule size and distribution at a given emulsifier content in water/oil emulsion and agitation speed. To eliminate the effects of the other factor, the agitation speed and emulsifier content were kept constant at 8000 rpm and 2 wt %, respectively. All of the microcapsules fabricated within the given range of polymer content were perfectly spherical in shape and well covered with the polymer wall. The capsules prepared with 1, 3, and 5 wt % of polymer concentrations were about 2.6, 4.3, and 8.2 μm in average diameter, respectively. This tendency was associated with an increase in polymer solution viscosity with increasing polymer concentration. In general, high-viscosity liquids exhibit a greater resistance to breakage and deformation than that of low-viscosity fluids when they are stirred. Consequently, they form larger and more stable emulsion droplets compared to those of 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, the interfacial tension of the disperse phase exhibits an almost linear decrease with the logarithm of the emulsifier concentration. At a high concentration 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, higher emulsifier content would produce smaller droplets. When the emulsifier content increased from 1 to 2 wt % (Fig. 4), the average size of microcapsules fabricated decreased from 6.8 to 4.1 μm, as explained above. However, when the emulsifier content increased further to 4 wt %, the microcapsule size increased to 4.9 μm. The abnormal increase of capsule size with emulsifier content could be found again at other agitation speeds, as shown in Figure 5. The reason for that could be postulated that when the emulsifier content was too high in the water/oil emulsion, excess emulsifier was introduced, slightly increasing rather than decreasing the droplet size with the increase in the content attributed to a too-viscous medium.

Figure 6 shows that the average size of microcapsules is reduced with increasing stirring speed. 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 di-

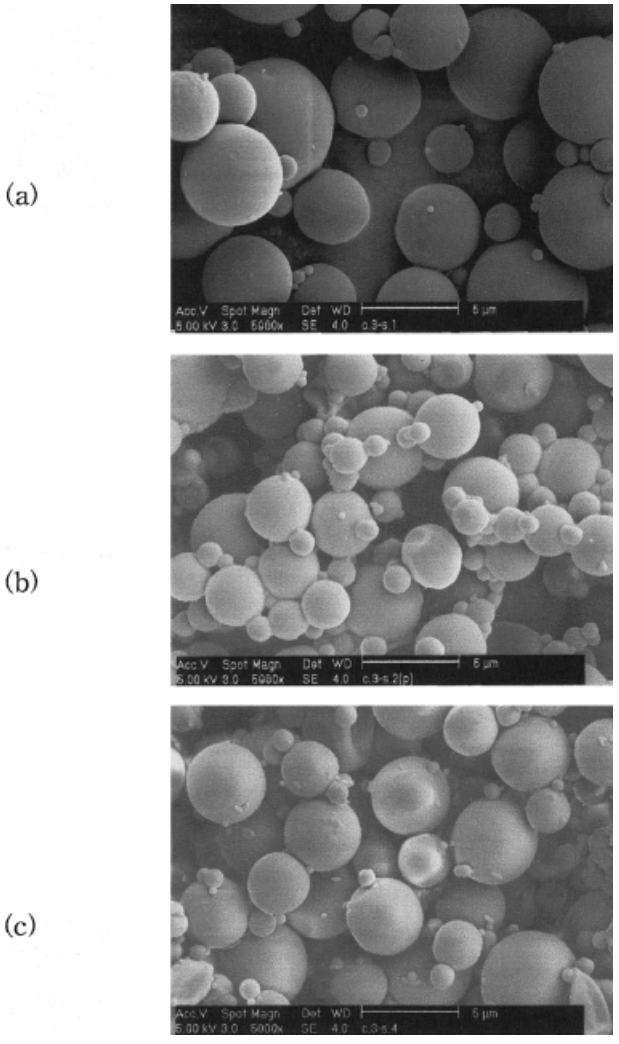

Figure 4 SEM photomicrographs of chitosan microcapsules prepared at different emulsifier contents in water/oil emulsion (polymer concentration = 3%, agitation speed = 8000 rpm): emulsifier content (a) 1 wt %; (b) 2 wt %; (c) 4 wt %.

rectly related to the shearing force. It was explained in the previous work that drop breakage in turbulent fields may be caused by viscous shear forces, by turbulent pressure fluctuations, or by relative velocity fluctuation. It is evident that as the agitation rate increases, the microcapsule size decreases to a limiting value.

Release Properties of Microcapsules

Figure 7 presents the release profiles of microcapsules prepared at different polymer concentrations in the aqueous phase. The amount of herbicide entrapped in the microcapsules was indirectly evaluated from the final herbicide concentration in the water phase when all of the herbicides were dissolved from microcapsules into the water. The microcapsules had release times ranging from 34 to 57 h and final herbicide concentrations of 7.9–17.4 ppm in the water, depending on the polymer concentration used in their preparation. As the polymer concentration increased, capsules with larger size and thicker capsule wall were formed, as observed in Figure 3, so that less herbicide could be entrapped and the release of the active material lasted for a longer time. In addition, larger capsules in the

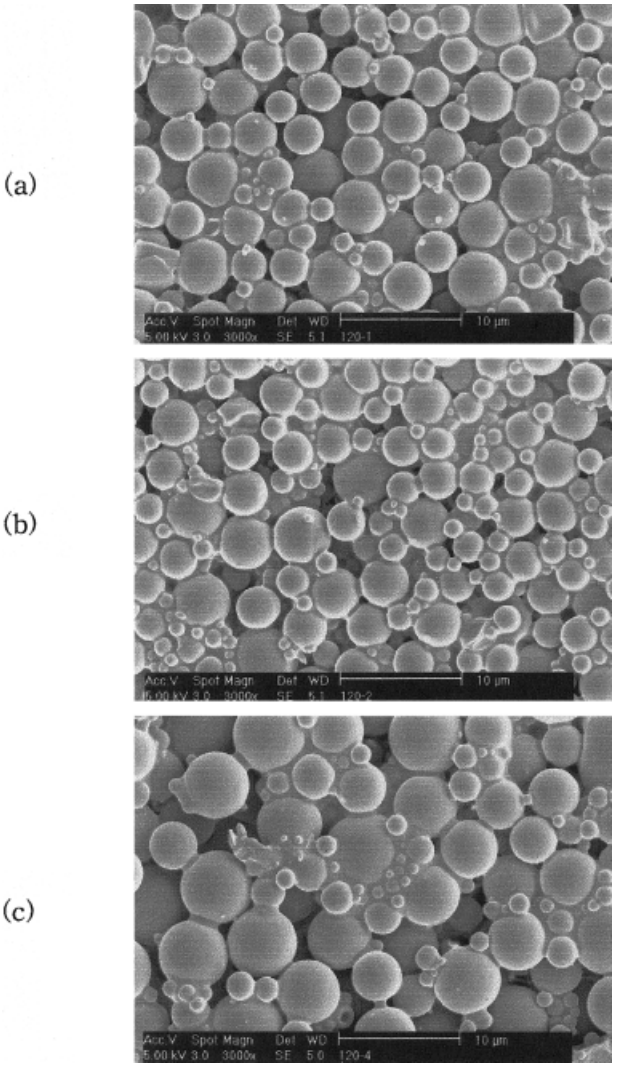

Figure 5 SEM photomicrographs of chitosan microcapsules prepared at different emulsifier contents in water/oil emulsion (polymer concentration = 3%, agitation speed = 12,000 rpm): emulsifier content (a) 1 wt %; (b) 2 wt %; (c) 4 wt %.

release system could be related to smaller surface area, which gave the slow release of the herbicide. The slower release of the herbicide could be explained in terms of the formation of larger capsules with thicker wall at higher polymer concentrations in the aqueous phase; permeation through a thicker layer and smaller surface area takes a longer time.

Figure 8 shows the release profiles of microcapsules fabricated at different emulsifier contents. It was discussed previously that the viscosity of the continuous phase as well as the interfacial tension of the disperse phase in the water/oil emulsion changes with emulsifier content and, thereby, the resulting microcapsule size can be determined, as shown in Figures 4 and 5. However, the microcapsules produced at different emulsifier contents have similar release properties and herbicide loading into microcapsule (release time = 90 h; final herbicide content in water = 21 ppm for all the microcapsules). It reflects that the microcapsules produced at different emulsifier contents have a similar capsule wall and herbicide amount encapsulated even though they are somehow different in size.

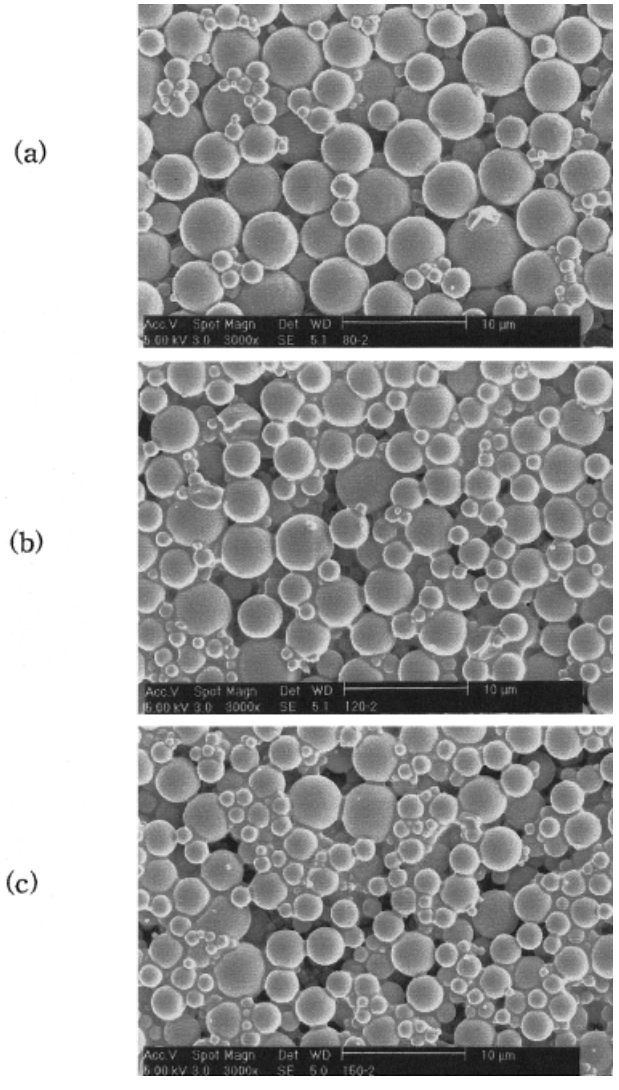

Figure 6 SEM photomicrographs of PVA microcapsules prepared at different agitation speeds (polymer concentration = 2 wt %, emulsifier content = 3 wt %): (a) 8000 rpm; (b) 12,000 rpm; (c) 15,000 rpm.

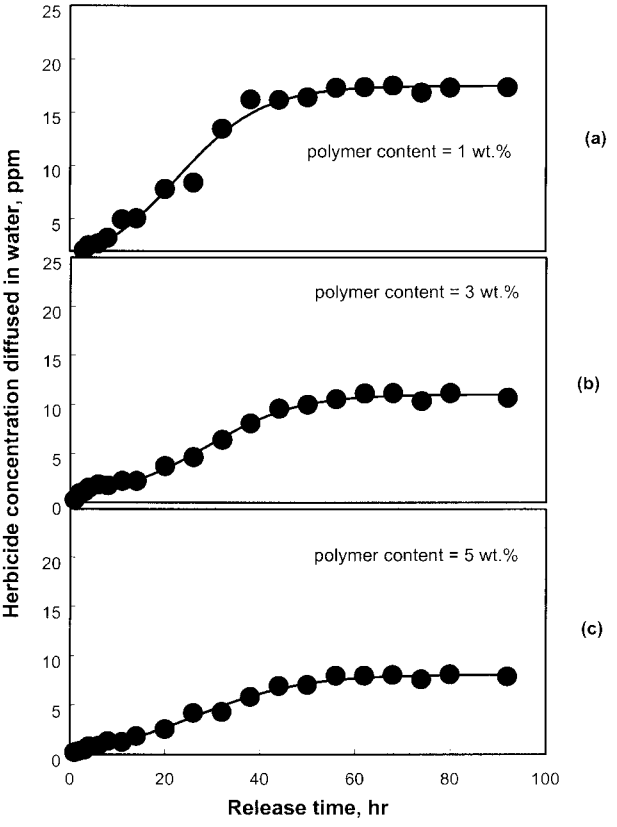

Figure 7 Release profiles of herbicide from chitosan microcapsules prepared at different polymer concentrations in aqueous polymer solution (agitation speed = 8000 rpm, SPAN 80 content = 2 wt %, release temperature = 30°C): polymer solution (a) 1 wt %; (b) 3 wt %; (c) 5 wt %.

Figure 9 exhibits the effect of agitation speed on release profiles of the fabricated microcapsules. As the agitation speed increased, the release profile shape changed considerably. When the agitation speed increases from 8000 to 15,000 rpm, the release time of the herbicide and final herbicide concentration in water increased significantly from 43 to 160 h and from 11 to 24 ppm, respectively. The reason for the changes is not

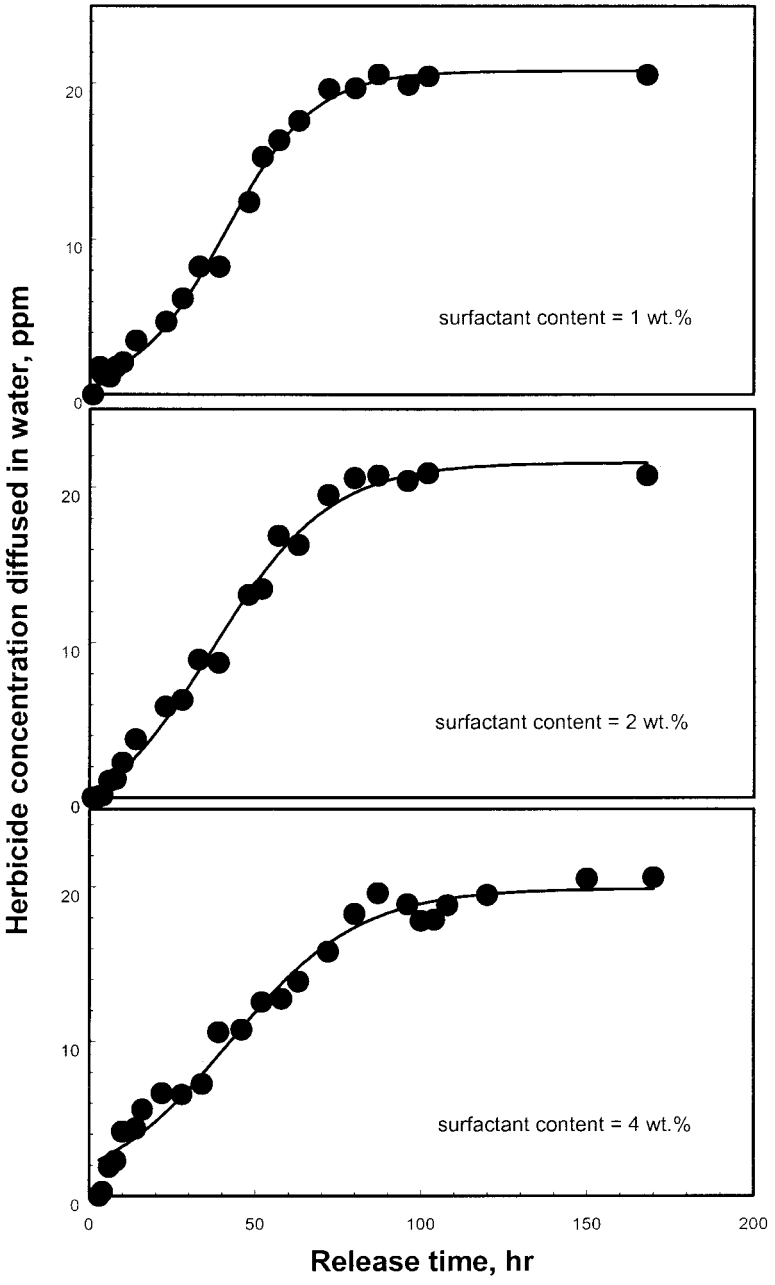

Figure 8 Release profiles of herbicide from chitosan microcapsules prepared at different emulsifier contents in water/oil emulsion: polymer concentration = 3%, release temperature = 30°C, agitation speed = 13,500 rpm.

clear but the longer release time for higher agitation speed might be explained in terms of the relation of capsule wall structure formed with shear force. Usually, the slow release through the capsule wall is characterized by the low mobility of the capsule wall. The low mobility of the wall material could be caused by a highly crosslinked structure or a compact structure. The former is not likely to be the case because all the capsules were subject to the same conditions for crosslinking kinetics. In other words, agitation speed can hardly affect crosslinking kinetics. Agitation creates shear force in a viscous fluid. The shear imposed on the polymer solution droplets will make polymer chains aligned to perpendicular to the shear direction, that is, parallel with the droplet

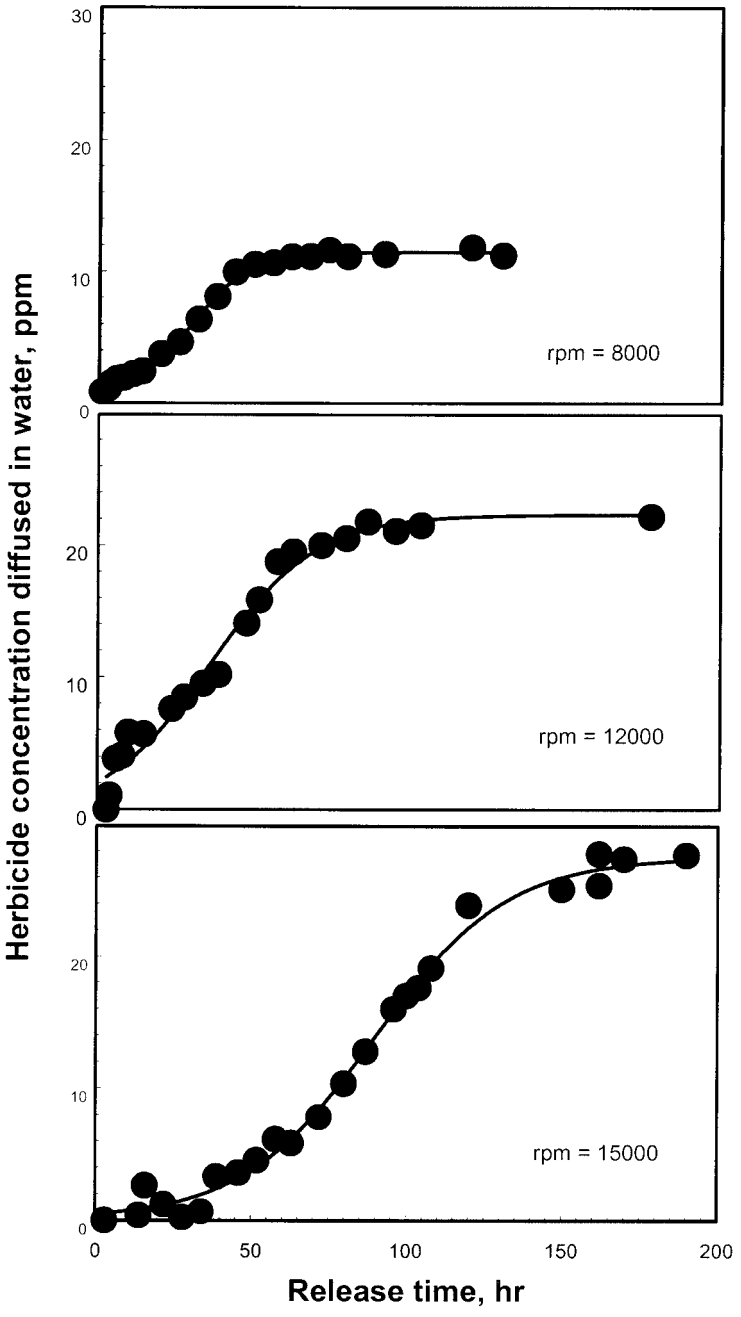

Figure 9 Release profiles of herbicide from chitosan microcapsules prepared at different agitation speeds: polymer concentration = 3 wt %, emulsifier content = 2 wt %, release temperature = 30°C.

surface. Therefore, the resulting capsules might have a dense and compact structure with low mobility. However, the relation between agitation speed and herbicide amount encapsulated needs to be investigated more. From these results, it can be seen that, among the three fabrication variables, agitation speed could most effectively control the both the rate of release and the herbicide amount encapsulated.

CONCLUSIONS

Chitosan microcapsules containing the water-soluble herbicide 3-hydroxy-5-methylisoxazole were

fabricated at different fabrication conditions by a new microencapsulation process established in the previous work.[6] In this study, the effects of fabrication variables were examined on the microcapsule size and distribution, encapsulation efficiency, and release properties. The polymer concentration in the aqueous phase determined the capsule size and capsule wall thickness by a resistance to breakage of the aqueous phase into droplets, which was related to the viscosity of the aqueous phase. The emulsifier concentration in water/oil emulsion was associated with microcapsule formation and the release properties of the prepared microcapsule by changing the interfacial tension of the disperse phase in breaking it into smaller droplets under a certain agitation. Under high agitation, the microcapsule formation is related to drop breakage in the turbulent field, which was caused by viscous shear forces, turbulent pressure fluctuation, and relative velocity fluctuation. The microcapsules prepared at an agitation speed of higher than 12,000 rpm were smaller than 5 μm in diameter, and the release of the active material from the capsules into pure water was sustained for 80–160 h, depending on the agitation speed used in microencapsulation. Among the fabrication variables, agitation speed could most effectively control both the rate of release and the herbicide amount encapsulated.

REFERENCES

1. Arshady, R. J Microencapsul 1989, 6, 13.
2. Morgan, P. W.; Kwolek, S. L. J Polym Sci 1959, 40, 299.
3. Wing, R. E.; Otey, F. H. J Polym Sci Polym Lett Ed 1983, 21, 121.
4. Shasha, B. S.; Trimnell, D.; Otey, F. H. J Polym Sci Polym Chem Ed 1981, 19, 1891.
5. Trimnell, D.; Shasha, B. S.; Wing, R. E.; Otey, F. H. J Appl Polym Sci 1982, 27, 3919.
6. Yeom, C. K.; Oh, S. B.; Rhim, J. W.; Lee, J. M. J Appl Polym Sci 2000, 78, 1645.
7. Mochizuki, A.; Amiya, S.; Sato, Y.; Ogawara, H.; Yamashita, S. J Appl Polym Sci 1989, 37, 3385.
8. Yeom, C. K.; Lee, K. H. J Membr Sci 1996, 109, 257.
9. Bachtsi, A. R.; Boutris, C. J.; Kiparissides, C. J Appl Polym Sci 1996, 60, 9.
10. Chatzi, E. G.; Kiparissides, C. Chem Eng Sci 1994, 49, 5039.
11. Koish, M. Chem Pharm Bull 1969, 17, 804.