# PREPARATION AND CONTROL RELEASE PROPERTIES OF POLYUREA MICROCAPSULE CONTAINING CYPERMETHRIN

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## 1. INTRODUCTION

Polymeric microcapsules are widely under investigation as pharmaceutical dosages, fragrant materials[1], pesticides, ink and so on. Cypermethrin is a kind of pesticides which have a variety of applications. Among the many methods, Interfacial reaction method is one of the most feasible and facile processes introducing immiscible oil-water phase. Therefore many interactions occur between oil and water phase, which affect the physical and chemical properties of the resultant microcapsules[2]. As typical model for interfacial reaction method, polyurea microcapsules have been studied plentifully on kinetics, effects of monomers and monomer compositions and various conditions of polymerization[3-5]. During the microencapsulation process by interfacial reaction, monomers in oil and water phases, respectively, diffuse onto the oil-water interface where they react with each other to form a polymer membrane[6]. In general, o/w emulsion is more useful to form microcapsules containing organic active materials as core, which can be achieved by mechanically dispersing the oil phase into water continuous watery phase. When o/w emulsion droplets are formed, the external water-soluble monomer diffuses across the water phase and reacts with the internal oil-soluble monomer to form a polymer membrane. Therefore, in this research we focused on the microencapsulation of cypermethrin as organic pesticide through interfacial reaction process based on the polymerization of diisocyanate and amine and investigated the effects of the protective colloids on microencapsulation.

## 2. EXPERIMENT

### (1) Materials

The monomers used in this experiment were TDI (toluenediisocyanate) and EDA (ethylenediamine) to form microcapsule wall in oil and water phase respectively. Both of them were purchased from Junsei chemicals Co. Ltd. Japan. Cypermethrin was obtained from LG chemical Co. Ltd. Korea, and its solvent, cyclohexane, was purchased from Junsei chemicals Co. Ltd. Japan. PVA (polyvinylalcohol, Mw ; 500) was purchased from Yakuri pure chemicals Co. Ltd. Japan and it is used as protective colloids.

### (2) Microcapsule preparation

Polyurea microcapsules were formed in this experiment by carrying out an interfacial polymerization reaction in an O/W emulsion between TDI dissolved in cyclohexane and EDA dissolved in water. Firstly, we acquired an organic mixture containing 8.6g of TDI and 0.2g of cypermethrin in cyclohexane, than water mixture was acquired by dissolving 0.05mol of EDA in distilled water. In 1000ml beaker, 200ml aqueous solution containing protective colloid was poured in it and then organic mixture was added with vigorous agitation. After agitating for 3 min, the water mixture was added into the resultant O/W emulsion to initiate polymerization reaction between TDI and EDA at the oil-water interface. And then the oil droplets were encapsulated to form the microcapsules. The temperature were elevated up to 70℃ to improve the reaction and maintained to the end for 3hrs. After 3hrs later, the microcapsule suspension was cooled and washed with water repeatedly and then filtered and finally, after drying with vacuum at room temperature for 24hrs, polyurea microcapsule powders were achieved.

### (3) Characterization analysis of polyurea microcapsules

Thermogravimetric analysis(TGA) was carried out on (TGA 5920, TA Co., USA) to investigate the thermal properties of microcapsules. Each sample was heated at the rate of 10℃/min up to 500℃ under constant $N_2$ flow. Mean particle size and distribution of microcapsules were determined with a particle size analyzer (Gali CIS-1 particle size analyzer, Israel). The shape and morphology of microcapsules were investigated by a scanning electron microscope (Hitachi S-4200, Japan). And finally release behavior of microcapsules was studied with UV-Vis spectrophotometer (UV-1601, Japan).

## 3. RESULTS AND DISCUSSION

### (1) Particle size

Fig.1 shows particle size distribution of polyurea microcapsules prepared from 0.2% and 4.0% PVA solution. The distribution became more uniform with increasing concentration of PVA solution. It indicates that the emulsion globules generated from high concentration were more stable and uniform than low one to form strong membrane walls.

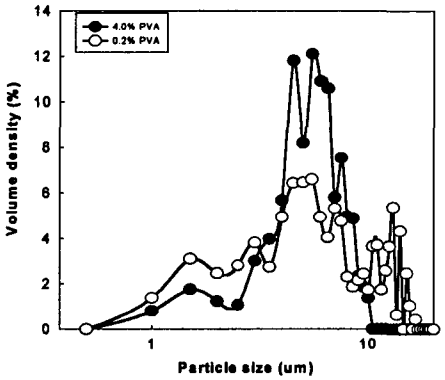
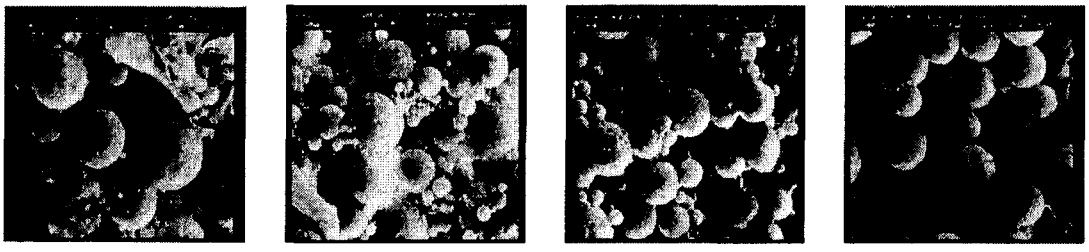



Fig. 1 Particle size distribution of polyurea microcapsules containing Cypermethrin from different PVA concentrations.

### (2) SEM photographs

Fig.2, SEM photographs of polyurea microcapsules from different concentration of PVA are shown respectively. The surface morphologies of microcapsules appeared to be spherical and stable. In low concentration, the size distribution of microcapsules was not uniform. This can support the previous result for the particle size distribution. Namely as the PVA concentration became higher, the particle size distribution appeared more uniform.



(a) 0.2% (b) 0.5% (c) 2.0% (d) 4.0%

Fig. 2 SEM photographs of polyurea microcapsules containing cypermethrin from different PVA concentrations. (a) 0.2%, (b) 0.5%, (c) 2.0%, (d) 4.0%

### (3) Thermal properties

Fig.3 show the TGA diagrams of the microcapsules from different PVA concentrations. All of the samples showed the first weight loss about 10% starts between 200-220℃ and the weight loss at a decomposition state approached at approximately 80% of the original weight at 340℃. In high concentration, the portions (-OH in PVA) which interact with free water become greater and this increases the frequency of the interactions between -NCO and $-NH_2$ to form urealinkages at the microencapsulation process. From the results of thermal analyses, it has also been confirmed that the protective colloids condition such as the internal structure and the concentration can control the physical properties of the microcapsules.

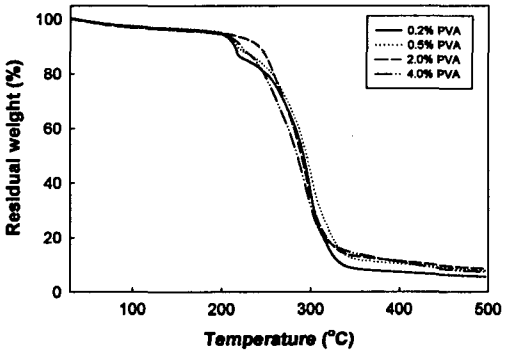



Fig. 3 TGA diagrams of polyurea microcapsules containing Cypermethrin from different PVA concentrations.

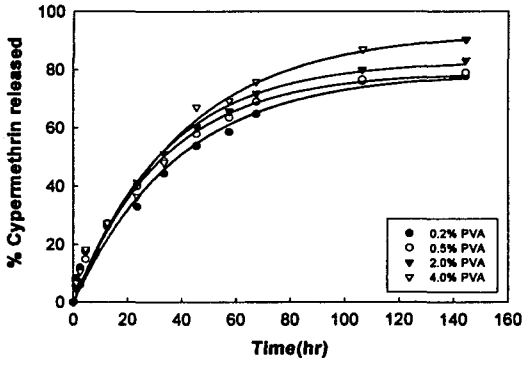



Fig. 4 Effect of PVA concentration on the release rate of cypermethrin from polyurea microcapsules.

### (4) Release properties

Fig.4 show the release behavior of polyurea microcapsules containing cypermethrin. As shown in the profiles, the release rate of cypermethrin according to the time became faster as the concentration of PVA solution increases. This can be explained by the particle size properties of the respective samples. In the high concentration, as the mean particle size is smaller and the distribution is more uniform, the cypermethrin could be released with easy for higher specific surface area. However, in the low concentration, because of the broad size distribution and somewhat large particle, it is shown that the release rate is decreased slightly for relatively lower specific surface area. Therefore the particle size properties such as size distribution and mean size are determined to be an especially important factors in controlling the release rate of core material in the

microcapsules. And furthermore, it is confirmed that the wall membranes prepared by PVA solution for protective colloids show more controlled and sustained release behavior. This may be due to the stability and strength of internal membrane structure of microcapsule as explained before.

## 4. CONCLUSIONS

Polyurea microcapsules containing cypermethrin were prepared by interfacial polymerization from TDI and EDA and their characterizations were investigated on the effects of protective colloids. From the results of particle size properties, SEM examinations and thermal analyses, it was determined that protective PVA colloid acted on the formation of microcapsule particles that had different properties. It was confirmed that the internal structure and concentration of protective colloids affected the reaction conditions, such as the stability of initial membrane and the reaction rate and consequently the polymer membrane that had different strength and property was formed. So it was indicated that the resultant microcapsules have different mean particle size, particle size distribution, and thermal stability of wall membrane. Furthermore, the differences in particle size distribution and morphologies influenced the release profiles of the core material from the membrane.

## REFERENCES

1. K. Hong and S. Park, Materials Chemistry and Physics, 58 (1999) 128-131
2. Peihong Ni, Mingzu Zhang and Nianxi Yarn, Journal of Membrane Science, 103 (1995) 51-55
3. Ki-jeong Hong and Soo-min Park, Materials Research Bulletin, 34, 6 (1999) 963-969
4. K. Hong and S. Park, Materials Science and Engineering, A272 (1999) 418-421
5. K. Hong and S. Park, Journal of Materials Science, 34 (1999) 3161-3164
6. S. K. Yadav, Kartic C. Khilar and A. K. Suresh, AIChE Journal 42, 9 (1996) 2616-2626