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〈Research Paper〉

# Effects of Protective Colloids on the Formation of Polyurea Microcapsules

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**Abstract**— Cypermethrin-containing polyurea microcapsules were prepared by interfacial polymerization using aromatic 2,4-toluene diisocyanate(TDI) and Ethylene diamine(EDA) as wall forming materials. The effects of the protective colloids of polyvinylalcohol(PVA) and gelatin were investigated through experimentation. The mean size of the polyurea microcapsules was smaller and the surface morphology of the PVA was much smoother than gelatin. In addition the release behavior was much more controlled and better sustained. As the concentration of protective colloid increased, the wall membrane of the polyurea microcapsules became more stable, the thermal stability of the wall membrane increased, the mean particle size became smaller, and the particle distribution was more uniform. The release behavior of the core material changed according to the concentration. As the gelatin concentration was increased, a more controlled and sustained release behavior was observed. However, in the case of PVA, the increase of PVA concentration lead to a more rapid release rate.

**Keywords:** *microcapsule, polyurea, PVA, gelatin, release behavior*

## 1. Introduction

Polymeric microcapsules are under wide investigation for practical uses such as pharmaceutical dosages, fragrant materials[1)], pesticides, ink, and so on. Cypermethrin is a kind of pesticide[2)] which has a variety of applications.

It controls a wide spectrum of insects, particularly Lepidoptera in cereals, citrus, forestry, soybeans, tomatoes, fruits, vegetables, vines, tobacco, cotton, coffee and other crops. It is yellowish brown, viscous, and semi-solid at ambient temperature and is highly soluble in an organic solvent such as cyclohexane.

Microencapsulation methods can be divided into three major categories : a physical method, a phase separation method, and an interfacial reaction method. Among these methods, the interfacial reaction method is the most feasible and facile method for introducing immiscible oil-water interfaces. This method can which affect the physical and chemical properties of the final microcapsules[3-7)].

During a microencapsulation process that uses the interfacial reaction method, monomers in the saving oil and water phase diffuse into the oil-water interface where they react with each other to form a polymer membrane[8-10)].

In general, O/W emulsion is more useful in forming microcapsules containing oily active materials as their core, and it can be achieved by mechanically dispersing the oil phase into water continuous phase[11)]. When O/W emulsion droplets are formed, the external water-soluble monomers diffuse across the water phase and react with the internal oil-soluble monomer to form a polymer membrane. As the reaction progresses, the membrane gradually strengthens and thickens to form a hard wall.

So the final properties of microcapsules greatly depend on the stability of o/w emulsions to stand mechanical agitation, the membrane of the droplets breaking up, and aggregations taking

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place between the membranes of the respective droplets.

In our research, we focused on the microencapsulation of pesticide oils and cypermethrin. The interfacial reaction based on the polymerization of TDI and EDA was also investigated to evaluate the influences of the protective colloids on microencapsulation.

## 2. Experimental

### 2.1 Materials

The monomers used in this experiment to form the microcapsule wall in the oil and water phase were ethylenediamine(EDA) and 2,4-toluene-diisocyanate(TDI). Both 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. Finally polyvinylalcohol(PVA, DP ; 500) was purchased from Yakuri pure chemicals Co., Ltd., Japan. and they were used as protective colloids. All the purchased chemicals and the reagents were used without any further purification.

### 2.2 Preparation of the microcapsules

Polyurea microcapsules were formed by carrying out an interfacial polymerization reaction in an O/W emulsion between TDI dissolved in cyclohexane and EDA dissolved in water. The oil phase formed the dispersed phase. All reactions took place in ambient temperature. An organic solution, with 8.6g of TDI in cyclohexane and dissolved 0.05mol of EDA in distilled water, was used as wall-forming materials. In addition 0.2g of cypermethrin was used as the core material, and PVA and gelatin in different concentrations were used as the protective colloid. The O/W emulsion was formed by adding the organic solution 200ml aqueous solution containing protective colloid, and then the mixture was stirred for three minutes. The EDA solution was then added the O/W emulsion after stirring for fifteen minutes to prevent agglomeration between the microcapsules. The temperature was increased to 70℃ to facilitate the reaction and was maintained at 70℃ for three hours. The microcapsule suspension was cooled and washed with 10% ethanol to remove the unreacted isocyanates on the surface, and then filtered and dried in a vacuum oven at 25℃ for twenty four hours.

### 2.3 Characterization of the Microcapsule

The infrared spectra of the core material and microcapsules was observed using a computerized Nicolet Impact 400D Fourier transform infrared(FTIR) spectrophotometer. A thermogravimetric analysis(TGA) was carried out on a DSC Mettler TA-3000(Thermal Science PL-STA). Each sample was heated at the rate of 10℃ /min up to 500℃ under a constant $N_2$ flow. The mean particle size and distribution of the microcapsules were measured with a particle analyzer (Galai CIS-100, Galai Production Ltd., Israel). The shape and morphology of the microcapsules were examined using a scanning electron microscope(SEM, Hitachi S-4200, Japan). Finally the release behavior of the microcapsules was observed with a UV-Vis spectrophotometer(UV-1601, Japan).

## 3. Results and Discussion

### 3.1 FT-IR Spectra

The FTIR spectra of pure TDI as the wall forming material, with cypermethrin as the core material and the microcapsules, are presented in Fig. 1. As seen in Fig. 1, the spectra show adsorption bands at 3400$cm^{-1}$ for the N-H stretching, and 1700$cm^{-1}$ for the C=O stretching of in the urea formation. The IR spectra also indicates a completion of the reaction of TDI with EDA by a disappearance of 2260$cm^{-1}$ of NCO by pure TDI, and the appearance of NH absorption band. In particular, the over CH stretching vibration is shown at 2900$cm^{-1}$ for the aliphatic methylene group of

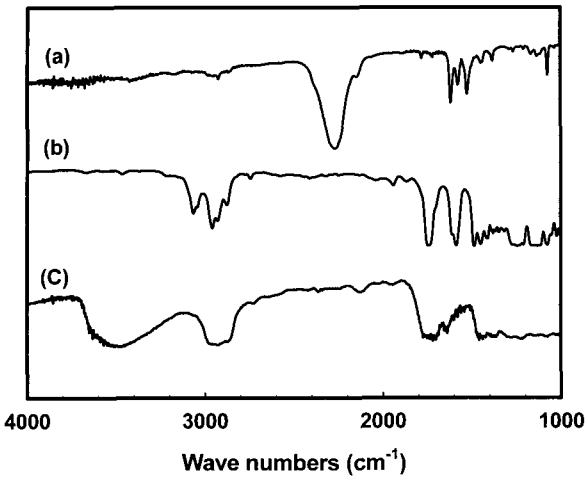



Fig. 1. FT-IR spectra of pure TDI(a), cypermethrin(b), and polyurea microcapsules(c).

diamines and C=O adsorption bands.

Therefore it can be confirmed that the core and wall materials of the microcapsules consisted of polyurea and cypermethrin.

## 3.2 Particle Size Distribution

Fig. 2 and 3 show the mean particle size of polyurea microcapsules containing cypermethrin in the presence of a protective colloids solution from different concentrations of gelatin solution and PVA. As shown in Figure 2, when the concentration of gelatin is increased from 0.1% to 2%, the mean particle size of the microcapsules is uneven. That is to say, in this case the particle size of the thinner (0.1, 0.5%) side of the gelatin appears smaller than the thick (1.0, 2.0%) side, and particularly in a solution of 0.5% there appears the smallest mean particle size. This is related to the stability of the emulsion globules and the initial membrane in the beginning of the reaction. In the case of a thinner solution, when the initial membrane was formed using polyurea, the stability of the membrane was so weak that it couldn't bear the mechanical stirring and finally the membrane broke into pieces or aggregation took place between the emulsion globules. So, the smaller particles might have been membrane fragments broken by the stirring.

In Fig. 3, according to the concentration of PVA, the mean particle size of polyurea microcapsules decreased from 7.15 to 5.68㎛ gradually.

This is also related to the fact that, in addition to what was explained above, PVA is more suitable to make small particles than gelatin.

A lot of hydroxy groups of PVA interact with $H_2O$ and these hydrogen bonds affect a rapid reaction with NCO and $NH_2$ to decrease the interaction between unbounded water and NCO. The initial membrane is more stable and stronger. So consequently smaller and more uniform particles can be formed rather than those formed using gelatin.

The particle size distribution of polyurea microcapsules prepared using 0.2% and 4.0% PVA

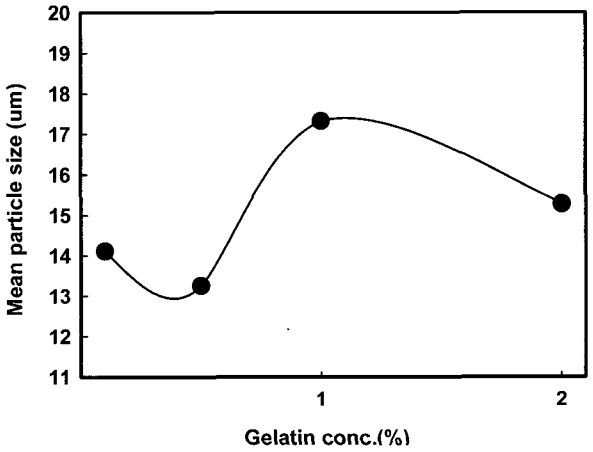



Fig. 2. Mean particles size of polyurea microcapsules prepared with different gelatin concentrations.

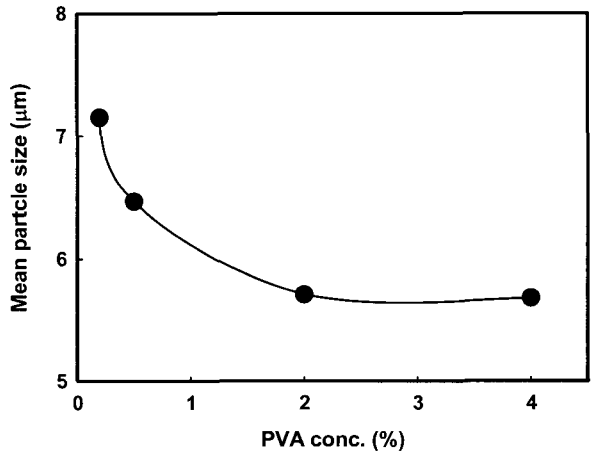



Fig. 3. Mean particles size changes of polyurea microcapsules prepared with different PVA concentrations.

solutions are shown in Fig. 4. As the concentration of PVA in the solution increased, the size distribution became narrower. This is caused by the fact that the addition of a high concentration of PVA emulsion resulted in strong membrane walls. This was due to a rapid polycondensation caused by a lot of hydroxyl groups which protected the interaction between unbounded water and NCO.

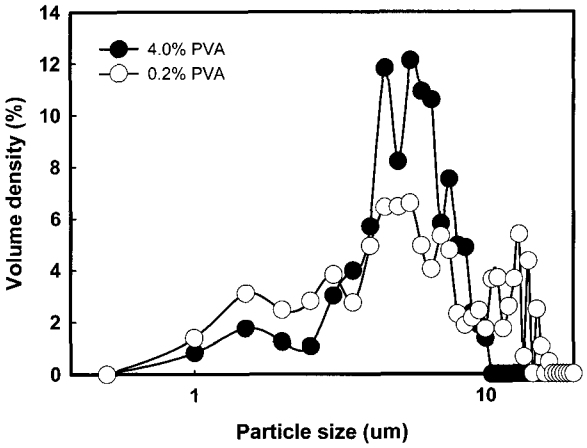
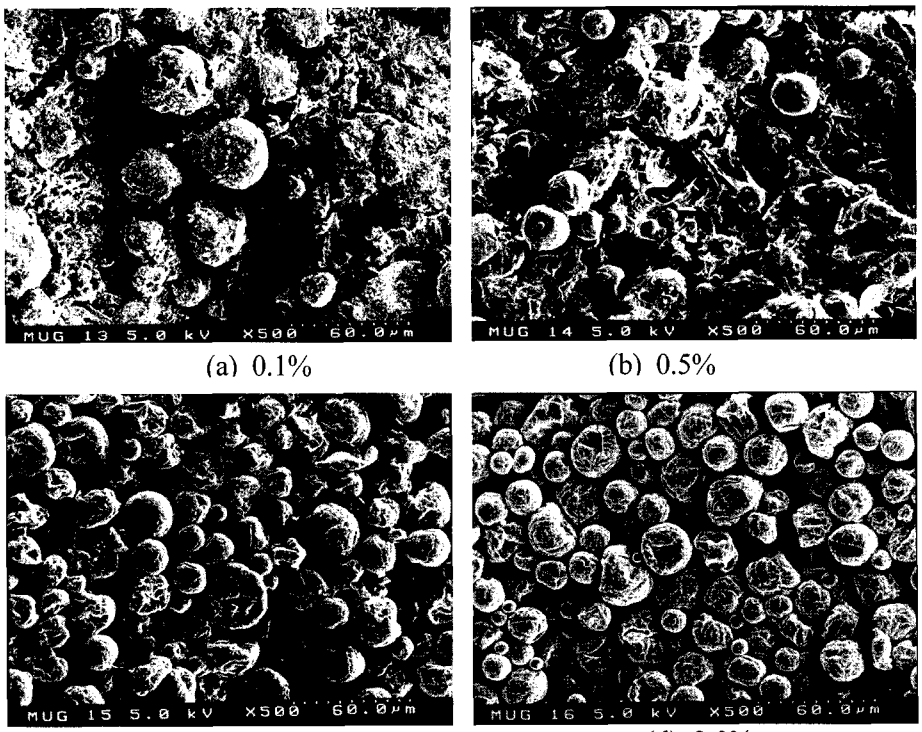



Fig. 4. Particles size distribution of polyurea microcapsules containing Cypermethrin from different PVA concentrations.

## 3.3 Morphology of Microcapsules

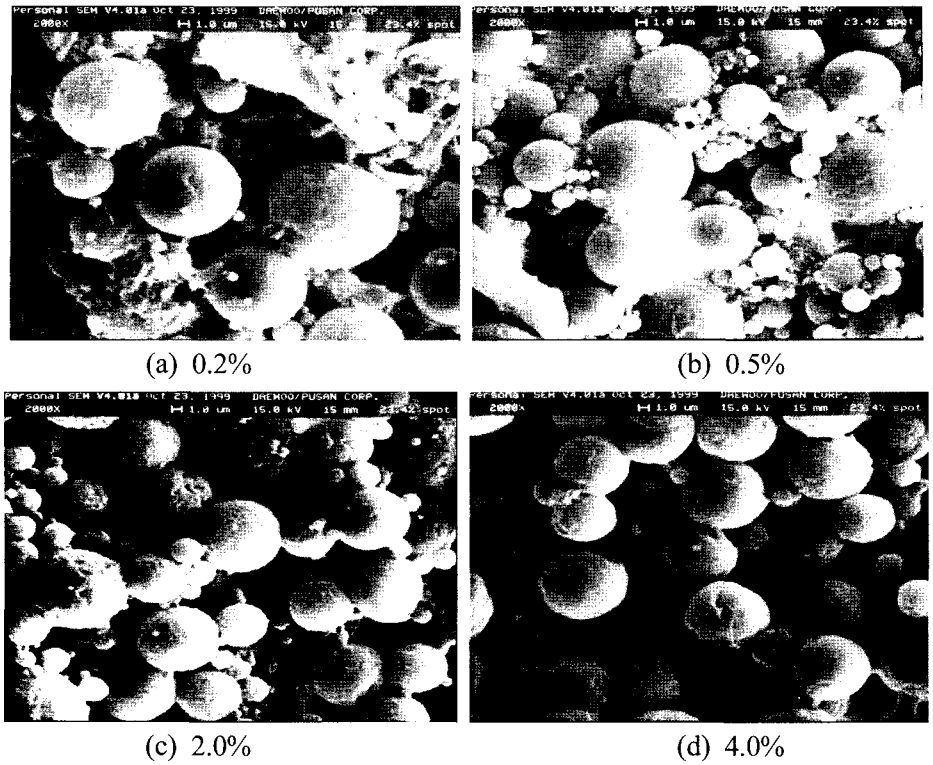
SEM photographs of the microcapsules containing cypermethrin prepared from the protective colloid with gelatin, and those with PVA, are shown Fig. 5 and 6, respectively. In Fig. 5, the morphology of microcapsules prepared according to the concentration of gelatine were more stable, uniform and spherical. Also, it has been shown that the microcapsule surfaces were extremely rough and had multiple cavities and cracks when prepared with a low concentration of gelatin. Many fragments are separated all around, which indicates that the initial wall strength was so weak that it couldn't bear the strong stirring. These results may affect the release properties through microcapsule membranes. In Fig. 6, the surface morphology of the microcapsules appear to be more spherical and stable compared with the case of those using gelatin as a protective colloid. In a concentration of below 1% PVA, the size and distribution of the microcapsules




(a) 0.1% (b) 0.5%

(c) 1.0% (d) 2.0%

Fig. 5. SEM photographs of polyurea microcapsules prepared with different gelatin concentrations. (a) 0.1%, (b) 0.5%, (c) 1.0%, (d) 2.0%



(a) 0.2% (b) 0.5%

(c) 2.0% (d) 4.0%

Fig. 6. SEM photographs of polyurea microcapsules prepared with different PVA concentrations. (a) 0.2%, (b) 0.5%, (c) 2.0%, (d) 4.0%

were not uniform, namely the bigger microcapsules and the smaller microcapsules were mixed together. This can support the previous results for the particle size distribution. In other words, as the PVA concentration becomes higher, the particle size distribution becomes more uniform.

## 3.4 Thermal properties

TGA diagrams show the thermal stability of the microcapsules prepared from gelatin and PVA. Fig. 7 and 8 show the TGA diagrams of the microcapsules prepared from the two different protective colloids using gelatin and PVA, respectively. All samples showed that the first weight loss of about 80% occurred in the temperature range from 220℃ to 340℃, and the second weight loss of 7 to 10% occurred, in the concentration of gelatin, up to 500℃.

The first weight loss was considered to be due to the melting of the polymer wall followed by the decomposition of the cypermethrin core materials. The residual weight of each sample became greater with the increase in the concentration of gelatin. This is related to the membrane structure and physical properties. As the concentration of gelatin increased the portion of CONH in gelatin and OH in PVA, which interacted with the free water, became greater, As s result this increases the frequency of the reaction rate between -NCO and -$NH_2$ to form urea linkages during microencapsulation.

This leads to the formation a stronger membrane structure, resulting in thermal resistance.

These diagrams also indicate that the residual weight of the microcapsules prepared using gelatin is relatively higher than those prepared using PVA. It is supposed that the microcapsule with gelatin contains a relatively small amount of liquid core material (the weight loss is the same as in the case of the concentration of gelatin) and lots of fragments from breakage due to the weak formation of the initial membrane. In order words, the liquid/solid ratio becomes lower and the resultant residual weight was much slighter in TGA.

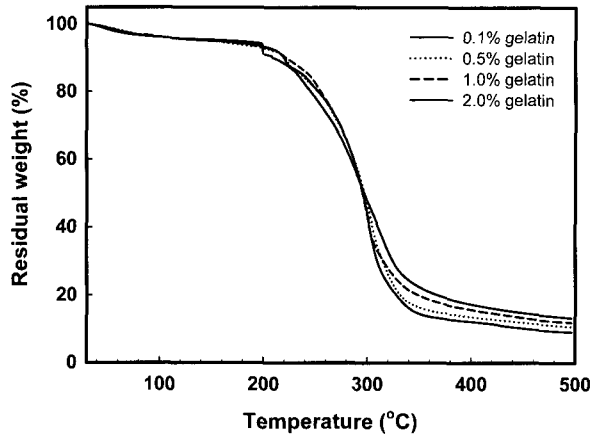



Fig. 7. TGA diagrams of polyurea microcapsules prepared with from different gelatin concentrations.

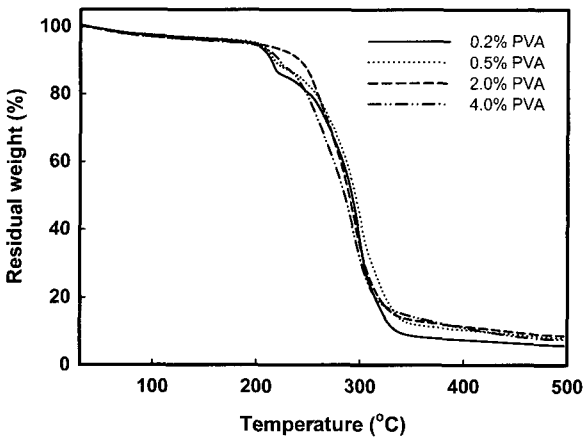



Fig. 8. TGA diagrams of polyurea microcapsules prepared with different PVA concentrations.

## 3.5 Release Properties

Release properties were investigated by releasing relative amounts of cypermethrin through a dialysis tube using a UV-visible spectrophotometer. 7mg of cypermethrin loaded polyurea microcapsules were suspended in 10ml of hexane and then put into the dialysis tube (Seamless Cellulose Tubing, Visking Company, Japan). The dialysis tube was placed into a 250ml bottle with 100ml of hexane, and the media was left while the temperature was kept constantly at 50℃. At specific time intervals, a sample was taken from each media, and the released amount of cypermethrin was determined by the UV-visible spectrophotometer at 250nm.

Fig. 9 shows the release behavior of the polyurea microcapsules containing cypermethrin formed using a gelatin solution for a protective colloid by polycondensation. It shows, as assumed from the results of the SEM photographs and examinations, that the release behavior through the microcapsules, membrane becomes more controlled and sustained with the increase of the gelatin concentration. These are related to the pores or cracks on the membrane surface.

The microcapsules are unstable in a concentration of under 1.0% gelatin because these cause the formation of pores or cracks on the membrane's surface. Therefore the apparent faster release rate in the beginning is due to the cypermethrin diffusing through the holes.

The release behavior of microcapsules prepared with a PVA solution is shown in Fig. 10.

These microcapsules , however, are in reverse order to those in the gelatin solution. As shown in the release profile, the release rate through the microcapsule's membrane, according

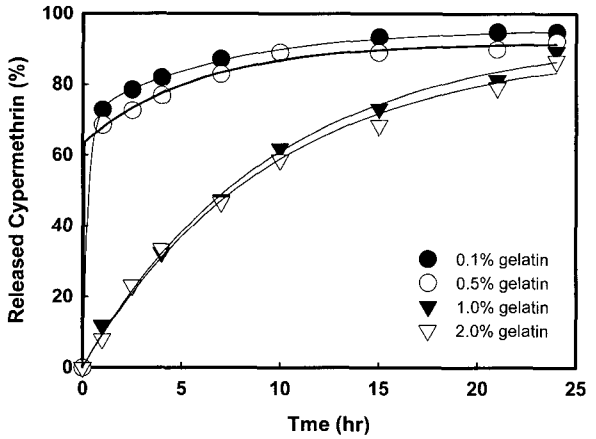



Fig. 9. Effect of gelatin concentration on the release rate of Cypermethrin from polyurea microcapsules.

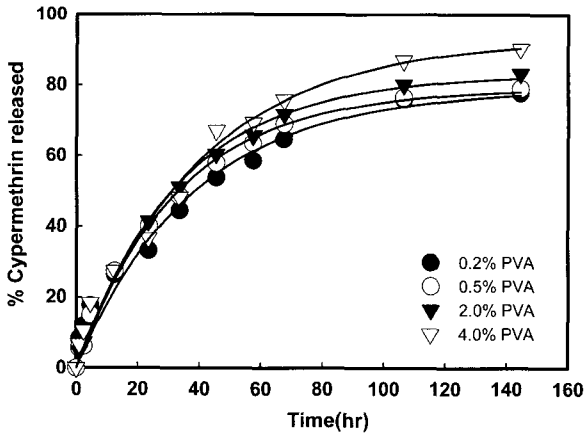



Fig. 10. Effect of PVA concentration on the release rate of Cypermethrin from polyurea microcapsules.

to time, becomes faster in relation to the concentration of PVA. This is related with the particle size properties, namely in a high concentration, as the mean particle size is smaller the distribution is more uniform. Thus the core material could be easily released due to a higher specific area. In opposition to low concentration, the broad size distribution and somewhat large particles decreased the release rate by their relatively lower specific area.

It is confirmed that the wall membranes prepared using a PVA solution for the protective colloid showed a more controlled and sustained release behavior. This may be due to the stability and strength of the internal structure as explained before.

## 4. Conclusions

Cypermethrin-containing polyurea microcapsules were prepared using interfacial polymerization with TDI and EDA, and their characterizations were investigated to evaluate the effects of the protective colloid. The mean particle size of polyurea microcapsules was smaller and the surface morphology was much smoother when PVA was used rather than gelatin. In addition, the release behavior was much more controlled and better sustained.

From the results of TGA and SEM it was abserved that polyurea microcapsules prepared using a protective colloid from PVA had a better particle size distribution, morphology and a longer release property compared to those prepared using gelatin.

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