

Effect of Trioctylamine on Microstructure of Water Containing Polystyrene Microcapsules

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Abstract. Microencapsulation technology has been used in a variety of fields including materials such as buildings, walls, industrial, medicine, and cosmetics. One of the most active research on microencapsulation is microstructure formation. Important properties of microcapsules such as releasing rate of active agent are depending on their microstructure. Same as the strength of bridges, skyscrapers, and buildings is characterized by their geometry, and the strength of microcapsules is also influenced by their microstructure. The effect of trioctylamine on the morphology of polystyrene microcapsules was investigated. The influence of trioctylamine was on both the inner and outer morphology of microcapsules. On outer morphology, two types which are smooth and crown were observed. Three types of inner morphology of microcapsules were classified. The inner morphologies are evenly spaced, clustered, and randomly spaced. The morphologies of the crown and evenly spaced were small in size.

Keywords: Polystyrene microcapsules \cdot Surface morphology \cdot Solvent evaporation method \cdot Trioctylamine

1 Introduction

A heterogeneous system is created in most cases of microcapsules applications. Therefore, the outer morphology of microcapsules has an essential role in the interface between medium and microcapsules during their interactions. In the beginning, a microcapsule is used for stable release which has a huge impact on the drug delivery system [1]. Later microcapsule containing drug was combined with a selective group that can connect special sites of receptors [2, 3]. That selective group can create a connection between the drug delivery system and the receptor. Nowadays, the microcapsule itself can be a mimic of protein for the target receptor. Microcapsule is possible to entrap active agents which have hydrophobic or hydrophilic after obtaining microcapsules with desired structure or shape [4]. Owing to obtaining desired shape and structure, the formation of various shapes and structures should be carefully examined under influencing factors.

The study is aiming to investigate the effect of trioctylamine on the morphology of polystyrene microcapsules. The preparation of microcapsules was conducted at first. Then, a size distribution of microcapsules in presence of trioctylamine was examined. Finally, the morphology of microcapsules with trioctylamine was evaluated.

2 Experimental

2.1 Reagents

Polyvinyl alcohol with 98.5% hydrolysis (PVA, polymerization degree: approximately 500), polystyrene (PS, polymerization degree: approximately 2000), trioctylamine (TOA), calcium chloride, and 1,2-dichloroethane (DCE) were purchased from Wako Pure Chemical Co.

2.2 Preparation of Microcapsules

The preparation scheme of the microcapsule is illustrated in Fig. 1. The microcapsules were prepared via a solvent evaporation method. The preparation conditions of the S/O suspension and the S/O/W emulsion were the same as in our previous work [4]. The S/O/W emulsion was stirred, as demonstrated in a previous paper [1, 5, 6], at 370 rpm, with the continuous evacuation of solvent vapor at 7.2×10^2 mmHg and 313 K for 8 h. The microcapsules were separated with a vacuum pump. In order to prepare the microcapsule containing TOA, 20% of TOA in the polystyrene wall was added to the organic phase. All TOA was entrapped to microcapsules, the titration experiment was done based on our previous study [7].



Fig. 1. Preparation scheme of microcapsules for the microstructure investigation of polystyrene microcapsules.

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Fig. 2. Characterization of the microcapsules. L-distance between spot, h-height of crown, W-coverage of cluster.

2.3 Characterization and Observation of the Microcapsules by Optical Microscopy

The morphologies of the microcapsules were observed by digital microscopy (DM, VHX-600 system, KEYENCE Corp.). The microcapsule distributions were characterized via the Hough transform which is available in our previous work [5]. The microcapsule sampling was directly from a reactor by using a micropipette. The images were taken with 100 times magnification by optical microscopy. Using the developed algorithm, 175 images with 1600×1200 pixels were carefully collected without overlapping for the automatic diameter measurement.

The characterizations of microcapsules' morphology based on digital microscopy images are illustrated in Fig. 2. Due to avoid deviation of measurement on the sphere, all morphological characteristics, shown in Fig. 2, are measured near the center of the circle which is a projection of the sphere. The purpose of these kinds of characteristic parameters is to use only the explanation of the effect on microcapsules with TOA addition not for preparation conditions.

3 Results and Discussion

The internal structure of the microcapsule, which is prepared with and without TOA, is shown in Fig. 3. In our previous study, the multicore and monocore dominated micro-capsules were prepared via solvent evaporation method under the control of osmotic pressure of salt. The overall appearance of both cases is the same in Figs. 3IA and 3IIA.

3.1 Effect on Size Distribution

The diameter distribution of prepared microcapsules with TOA and control sample is plotted in Fig. 4. Coefficients of variation (ν) of the sample and control sample were 0.251 and 0.248, respectively. The mean diameter difference is only 6 μ m. Therefore, the population of microcapsules in presence of TOA is identical to the control sample population.

3.2 Morphological Observation

Two types of outer morphology and three types of inner morphology are observed in prepared microcapsules in presence of TOA (Fig. 5).



Fig. 3. Prepared microcapsules. I-control; II-sample with TOA; A-low magnification; B, C-higher magnification: same microcapsules with different focal planes (WS/O = 0.146 wt%).

Table 1. Size distribution of microcapsules by the Hough transform (WS/O = 0.146 wt%).

Parameters	Microcapsules with TOA	Microcapsules without TOA
Mean diameter (D) [µm]	122	116
Standard deviation (σ) [μ m]	30.6	28.7
Coefficients of variation (v) [–]	0.251	0.248



Fig. 4. Histogram of prepared microcapsules' size (WS/O = 0.146 wt%).

Inner Morphology

Clustered Type. The appearance of clustered type morphology is shown in Fig. 6. An occurrence of a cluster of inner droplets is on the monocore microcapsule. One big



Fig. 5. Various types of morphologies in population of microcapsules with TOA. A-cluster type, B-evenly spaced type, C-randomly spaced type, D-crown type.



Fig. 6. Cluster type. A, B-focus on the side; A^l , B^l -focus on the front; C - front view, D - side view, Z-wall thickness.

ellipsoid is in the center and small spherical droplets are located around the ellipsoid. From observation of the side view, it has enough distance (L) compared to cluster coverage (W) and relatively strong big inner droplets, hence, small droplets can be formed a spherical shape because of enough space. But big droplets have ellipsoid shape because they are pushed by film from two sides. A graphical illustration of shape formation is shown in Figs. 6A, 6B, and 6D. Another piece of information from this shape is the stability of the bigger inner droplet in the center. It is indicated that TOA stabilizes the inner droplet enough under relatively high pressure. Therefore, external pressure has a role in the pressure equilibrium between the bigger ellipsoid and the small sphere. However, if the inner droplet still has an osmotic flow due to salt concentration, it is possible to escape or explode because of a size increase.

Evenly Spaced Type. The morphology of the evenly spaced type is shown in Fig. 5B. This type of morphology is observed in monocore microcapsule. Here many relatively uniform-sized inner droplets are distributed in the wall with a certain thickness. Between the inner and outer film, no small droplets were observed. Hence, Ostwald ripening is dominated over coalescence in this case. Inner and outer films serve as restricting devices such as pillars on the surface [8], but it is one dimensional (1D) case according to diameter. The increase of inner droplets is limited by wall thickness. If the osmotic flow continues, an escape of the inner droplet occurred to either outside or inside of the monocore microcapsule. Another feature of the evenly spaced type is the distance (L), which is small compared to clustered type, between inner spots. It is concluded that external pressure on the internal spot of this type is smaller than the ellipsoid of the clustered type. The Laplace pressure forces small spots to disappear in the liquid membrane system with TOA because external pressure on the spot is not enough for the smaller daughter distribution of droplets through the wall.

Randomly Spaced Type. The morphology of the randomly spaced type is shown in Figs. 3, and 5C. This type of morphology is observed in both monocore and multicore microcapsules. In this case, the formation of inner droplets does have not any restriction in space. Hence, inner droplets can be randomly sized and the shape is spherical. If wall thickness (\mathbf{Z}) is much larger than spot diameter (\mathbf{d}), space restriction is not counted. The randomly spaced type is the most dominant type, regardless of the TOA addition.

Outer Morphology

Crown Type. Morphological observation of crown type is illustrated in Fig. 7. The Crown which is a small sphere on the microcapsule is possible to from the outside and inside. If it is created from the inside, it should be an escape of the inner droplet. If it



Fig. 7. Crown type. B, C - same microcapsule but with a different focus.

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is created from the outside, it should be a collision of the small-sized spheres followed by cohesion on the surface of the microcapsule. In the last case, every microcapsule among the entire population should have small-sized spheres on the surface but it is not observed. Therefore, the formation of crown type is the escape of the inner droplet.

In normal cases, inner droplets tend to be located center, especially the bigger ones, however, the inner droplets of microcapsules with high curvature have a tendency to escape. It is true for both cases with and without TOA. The difference is going from the stability of the droplet film. The escape of the inner droplet without TOA has not a barrier of strong outer film. But the inner droplet is caught by the outer film on the surface in presence of TOA. A result is the formation of the crown type.

Smooth or Regular Type. If the outer morphology of the microcapsule is not the crown type, then it is classified as smooth or regular type. Here in this study, smooth-ness is comparable to the size of the crown height (\mathbf{h}). The outer morphology of cluster, evenly spaced, and randomly spaced types are classified as the smooth or regular type.

4 Conclusion

Trioctylamine has no effect on size distribution with the given conditions. But the morphology of microcapsules is influenced by trioctylamine. Various morphologies such as evenly spaced, clustered, and crown types including smooth and randomly spaced types were observed in presence of TOA. The Laplace pressure and the stability of droplets have played important roles in the formation of different morphologies with TOA. Only smooth and randomly spaced types of morphologies occurred in prepared microcapsules without TOA. The morphologies of the crown and evenly spaced were small in average size.

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