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A novel preparation method for capsules containing a high proportion of magnetite using a magnetic field

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Summary

The capsules containing magnetite has been used in several applications. Conventional methods for preparing capsules containing magnetite have not achieved a high rate of magnetite content. In this research, we succeeded in preparing capsules containing a high proportion of magnetite with a new method that uses a magnetic field. These capsules are prepared by interfacial polymerization of polyamide. The capsule size is controllable in the approximate range of 20-1000 μm. The method can possibly be used for even smaller capsules with improvement of apparatus. Calculation of density showed that the capsules contained magnetite at a rate of 50% or more. They are believed to be easily mass-produced and their industrial application is expected.

Introduction

Magnetite has been mainly used for recording materials including FDs. In recent years, research and application are evident in the biological and medical fields, including MRI contrast agent[1], DDS[2], and chemoembolization of cancer[3] and other. We too have studied the use of magnetite in display devices[4] and actuators[5]. In most examples of its utility mentioned above, contact between magnetite and objects is not preferred. Magnetite is mostly encapsulated before use[1-5].

Conventional methods for preparing capsules containing magnetite have not achieved a high rate of magnetite content. This is because magnetite cannot be retained in micelles in the emulsification process by mechanical agitation, due to instability of the magnetite surface condition. Consequently, a substantial amount of by-products other than capsules is produced. In addition, magnetite is not contained in all capsules and process yield remains low.

In the present research, we attempted to prepare capsules containing magnetite with a novel method that uses a magnetic field. Consequently, we succeeded in solving existing problems such as a low rate of magnetite content and poor process yield.

Experiment

Reagents and materials

Hexyltrimethoxysilane (Shin-Etsu Chemical, KBM-3063), chloroform, cyclohexane, hexamethylenediamine and telephthaloyldichloride (Nacalai Tesque) respectively were purchased, and used without purification. Distilled water was used as water.
Magnetite was prepared by coprecipitation, by employing the method of Shimoiizaka[6]. Prepared magnetite was surface-treated by wet process with hexyltrimethoxysilane.
For microscope observation, a stereomicroscope (Olympus SZ-series) and a biological microscope (Olympus BX-series) were used.
For the magnet, a rare earth magnet (neodymium magnet, surface inductive flux 0.5 T) was used.

The Preparation method of capsules containing magnetite

The principle of preparation is shown in Figure. 1. A droplet of organic solvent containing magnetite and telephthaloyldichloride is applied to a hexamethylenediamine water solution using magnetic force. The droplet reaches the surface of the hexamethylenediamine water solution. The magnetite and a small quantity of organic solvent on the surface of the magnetite then sink under the water solution, attracted by the magnetic field. This process produces a polyamide membrane[7] on the surface of the magnetite.

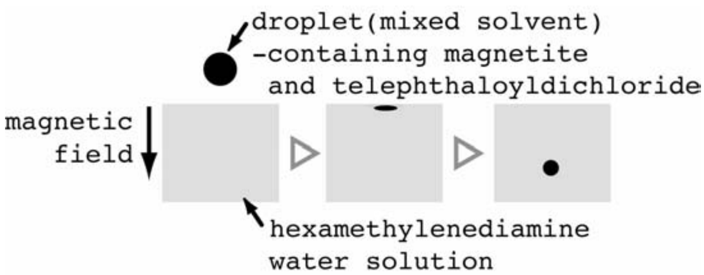

Figure.1 Schematic diagram of capsule preparation process.

The actual preparation was carried out as shown in Figure. 2. The diameter of the pipette tip and the distance between the magnetite and the pipette are hereinafter referred to as d_p and $D_{m\text{-}p}$, respectively.
An organic solvent containing magnetite and telephthaloyldichloride is prepared as the inner phase of the capsule and put in the pipette in advance. A hexamethylenediamine water solution is put in a petri dish as the outer phase of the capsule. A magnet is placed under the petri dish. Encapsulation was initiated by bringing the pipette close to the magnet.
An organic solvent phase was chosen for the inner phase of the capsule. A mixed solvent of chloroform:cyclohexane=1:4 (v/v) was used for this organic solvent[8]. The quantity of telephthaloyldichloride used was 0.25 mol/l. Magnetite with and without

surface treatment was used. The density of the magnetite was 20 wt% unless otherwise specified.

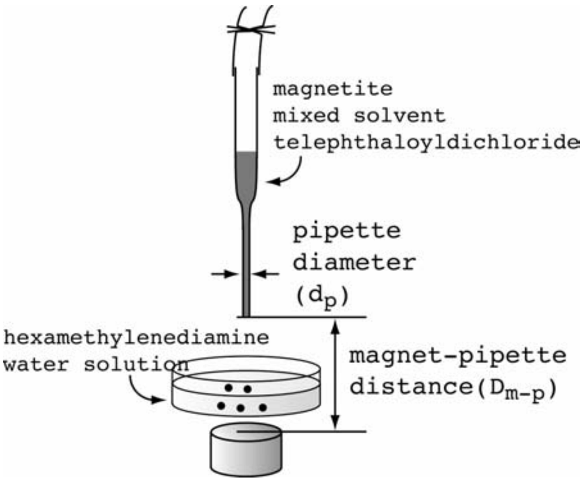

Figure.2 Method for preparing capsules.

A water phase was chosen for the outer phase of the capsule. As with the telephthaloyldichloride, the quantity of hexamethylenediamine used was 0.25 mol/l. Prepared capsules were washed with distilled water after reaction for a specified amount of time.

Results

Figure. 3 shows a photograph of a prepared capsule. Its diameter is approximately 950 μm. The preparation conditions of this capsule were d_p=1.0 mm and D_{m-p}=20 mm. The magnetite underwent processing with a silane coupling agent before use. The average particle diameter of capsules under these conditions was approximately 800 μm. Calculation of specific gravity showed the percentage of magnetite to be 50% or more.

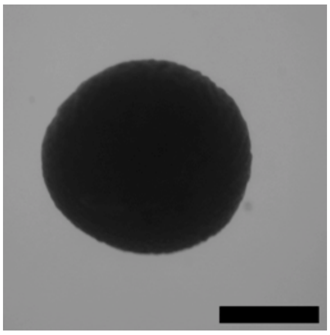

Figure.3 Photograph of a prepared capsule taken with a stereomicroscope. Scale bar shows 500 μm.

It was found that magnetite needs to be surface-treated, since the pipette tip became plugged with the magnetite when the surface of the magnetite was not treated. Besides, when the surface of the magnetite was not treated, the magnetite supply was unstable and the particle diameter exhibited a wide distribution. From these results as well, it is clear that the magnetite surface needs to be treated.

As d_p becomes small (1.0 mm to 0.3 mm), the average particle diameter becomes small (800 µm to 550 µm). At this point, blockage of the magnetite in the pipette tip became a problem. Consequently, the magnetite density was reduced (10 wt%). Although the reduced magnetite density solved the blockage problem, the supply of telephthaloyldichloride solvent solution increased. A superfluous organic solvent remained as a polyamide membrane on the surface of the hexamethylenediamine water solution. This polyamide membrane hindered the subsequent capsule preparation (see Figure. 4).

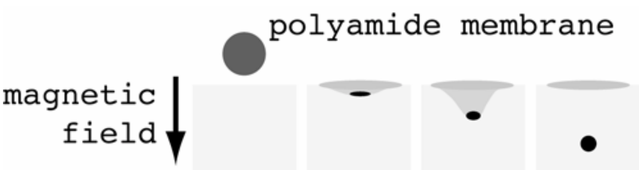

Figure.4 Schematic diagram of capsule preparation method. A case in which the amount of telephthaloyldichloride organic solvent solution supplied was excessive.

From the results obtained so far, the critical point of this method was recognizing how to achieve a stable supply of a small quantity of magnetite. Consequently, under the condition of d_p=1.0 mm and D_{m-p}=20 mm, the pipette was inclined at an angle of 45 degree. The inclination allowed the stable supply of a small quantity of magnetite. Figure. 5 shows the particle diameter distribution of capsules prepared by this method.

A narrow distribution of the particle diameter was exhibited. The average particle diameter was 380 µm.

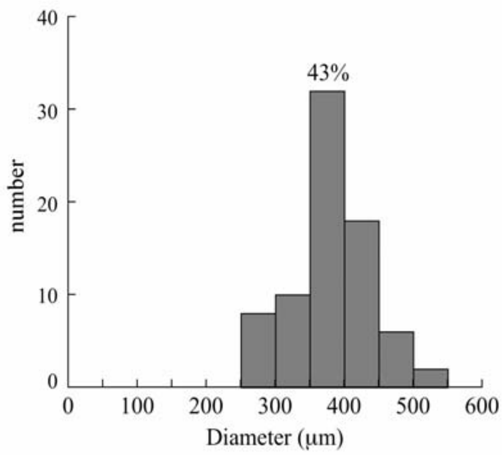

Figure.5 Particle size distribution of capsules. (d_p=1.0 mm, D_{m-p}=20 mm, supply pipe inclination angle = 45 degree)

However, as the supply was further reduced, the magnetic field force became insufficient to encapsulate the magnetite. This occurs because the sinking of magnetite is hindered by the polyamide membrane produced when the droplet reaches the solution. As shown in Figure. 6, a substance that failed to be encapsulated remained on the surface.

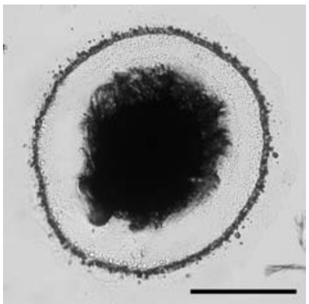

Figure.6 Suspended substance produced by insufficient magnetic field force. Scale bar shows 50μm.

Consequently, we attempted to obtain a sufficient magnet field force by reducing the amount of hexamethylenediamine solution under the pipette, to D_{m-p}=5.0 mm. D_p was 0.3 mm and the magnetite density was 20 wt%. Figure. 7 shows a capsule obtained in consequence. The diameter of this capsule was approximately 20 μm.

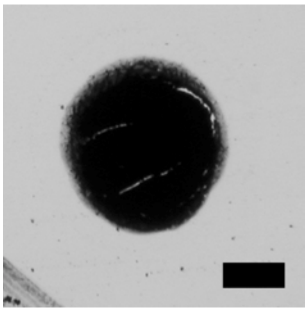

Figure.7 Capsule obtained by reduced D_{m-p} (D_{m-p}=5.0 mm). Scale bar shows 10μm.

It was found that preparation of minute capsules using this method requires a particular process of supplying magnetite and a sufficient application of the magnetic field. In addition, surface treatment of magnetite and magnetite density are also important for a stable magnetite supply, which needs to be thoroughly studied in the future.

Conclusion

It was shown that preparation of capsules containing a high proportion of magnetite is easily achievable using a magnetic field. The capsules were prepared by interfacial polymerization of polyamide. The capsule size is controllable in the approximate range

of 20-1000 μm. Calculation of density showed that the capsules contained magnetite at a rate of 50% or more.
Formation of fibers containing magnetite may also be possible by applying this method. It may be possible to use these capsules for the purposes mentioned at the beginning of this paper. In addition, due to the interfacial polymerization employed, this method provides high versatility, along with a wide range of applications in the future, since it can be used with various kinds of polymers. Furthermore, due to its simple process, it is suitable for serial production and is expected to provide high productivity.

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