다양한 고분자 물질을 이용한 방향(芳香) 미세 캡슐의 제조 및 특성

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Preparation and characterization of microcapsules containing perfumes with different polymer shells

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Introduction

Microencapsulation means the formation of small, coated particles loaded with a certain phase, such as solid, liquid, solid/liquid dispersion or gas. Microcapsules, usually between 1 and 1000 μm in diameter, consist of an adequate core and impervious shell only a few microns thick [1].

Current global microencapsulated product sales are estimated to be about 12～14 billion dollars per year with carbonless copy paper representing 7 billion dollars of this total. It is hard to estimate the accuracy of any of these numbers, however the key point is that microcapsule-based product sales are large and growing steadily. As such, it is the potential for this scale of product sales in a number of other capsule applications that continues to drive the development of microcapsule technology [2].

Microcapsules have been successfully used in a wide range of applications with great advantage. The examples include inks, dyes, chemical reagents, pharmaceuticals, flavoring agents, pesticides and adhesives. Since the encapsulated fills are protected from air, moisture, microorganisms, and other contaminants, spoilage is reduced and the shelf-life of the fill is increased [3].

Microcapsules can be prepared by three different methods; phase separation methods, chemical methods, and mechanical methods. In a phase separation-based process, the core contents in a solvent are first suspended in a solution of the shell material. The shell polymer is then induced to separate as a new, viscous, polymeric phase by adding a nonsolvent, lowering the temperature, changing the pH, adding a second polymer, or changing other environmental conditions. It is essential that such changes can drive the polymer to come out of the solution and aggregate around a core droplet to form a continuous encapsulating shell [4]. Chemical processes are normally performed in a liquid-filled stirred tank or tubular reactor. In general, it includes interfacial condensation polymerization, in-situ polymerization, interfacial addition polymerization, etc. [5]. Capsules produced by mechanical processes, so-called physical processes, utilize a gas phase at some stage in the encapsulation process. In such processes, capsules can be formed by either spraying droplets of the coating material on the core material being encapsulated, solidifying liquid droplets sprayed into a gas phase, gelling droplets sprayed into a liquid bath, or carrying out a polymerization reaction at a solid-gas interface. For each method, selecting different experimental conditions and polymer materials as the shell can produce various thickness, hardness, and aqueous solubility and molecular weight for the shell.

One method of preparing microcapsules is in-situ polymerization, where droplets are first formed by dispersing core ingredients into an aqueous phase containing a small fraction of an emulsifier. Following emulsification, the proper prepolymer is added and a polymeric shell forms rapidly around the droplets. The encapsulated particles must then be separated from the continuous phase by washing, filtering, and drying. In most applications, it is often desirable to have a narrow particle size distribution. The emulsification step is the primary determining step in establishing the size and size distribution of microcapsules. This step can be influenced by the physical parameters such as the mixer/vessel configuration, speed of mixing, and volume ratio of the two phases, and physicochemical

properties such as the surface tension of the emulsifier and chemical composition of the two phases in contact.

The objectives of the current research are to prepare microcapsules containing oily perfumes as the core and investigate the characteristics of these capsules such as the size, size distribution, and morphological properties. Accordingly, microcapsules within a range of 1～50 μm were prepared using an in-situ polymerization method in a batch-stirred reactor.

Experimental

Materials

Some different oily perfumes were obtained from Seil Perfume Co. (Korea) and used without further purification. The melamine monomer and formaldehyde used to form the capsule shells were supplied by Samsung Fine Chemicals Co. (Korea) and Aldrich (USA), respectively. Styrene-maleic anhydride-monomethyl maleate copolymer (SMA) produced by Monsanto (USA) was selected to emulsify the core material into an aqueous phase. All other chemicals were first-grade reagents from Oriental Chemical Industry (Korea), and used without further purification.

Encapsulation

The microcapsules were prepared using an in-situ polymerization method. The encapsulation process was divided into three individual steps, that is, an emulsifying step, prepolymer preparation step, and polymerization step.

(1) Emulsification

50 g of SMA powders was first added to 950 g of the distilled water, and the emulsifier of this yellowish solution was prepared by heating the mixture up to 90℃ over 3 hours and subsequent cooling to room temperature.

The emulsifying step was performed using a TK-homomixer (Mark-II 2.5, Tokushu Kika Kogyo Co., Japan). 200 g of fragrant oil was first added to 260 g of the emulsifier solution, and the mixture stirred by the homomixer within a range of 1000～10000 rpm for 7～12 minutes at room temperature [6].

(2) Prepolymer preparation

Dual-jacketed batch reactors with a working volume of 1 L were preheated by hot water circulated from a water bath set at 60℃. Various polymeric materials to prepare the capsule shell such as melamine-formalin, urea-formalin, and melamine-urea-formalin were added into the reactor simultaneously. By stirring over 600 rpm using a mechanical stirrer with a teflon-coated head, a semi-transparent prepolymer was obtained after a reaction time of 10～20 minutes.

(3) Polymerization

The emulsion prepared in the emulsifying step was added to the reactor containing the prepolymer. Polymerization was carried out at a reaction temperature of 60℃ and 600 rpm. To obtain capsules with good uniformity and better mechanical properties, the shape and size of the droplets in the emulsifying step as well as the capsules in the polymerization step were carefully be observed through out the encapsulation steps. After 3～4 hours from the start of the reaction, microcapsules were prepared containing perfumes as the core material and various polymeric resin as the shell material, which has the proper delivery characteristics. The encapsulation process is usually supplemented by an appropriate harding step to increase the intensity of the capsule shell.

Characterization of capsules

The particle size and size distribution of the capsules were determined using an optical microscope

(BX550 from Olympus) and FA particle analyzer (FRITSCH), respectively. The thermal properties of the capsules were examined using a differential scanning calorimeter (DSC: DSC550 from Instrument specialists Inc.). A scanning electron microscope (SEM) was also used to investigate the morphology of the capsules.

The measurements by the particle analyzer were carried out within a range of 0.10～601.48 μm under the resolution of a laser source from 9 to 228 mm.

The thermal properties of the capsules dried in a convection oven were also evaluated using a differential scanning calorimeter under a nitrogen atmosphere. Since it is known that the capsule size has no effect on the measured values of either the melting temperature or the latent heat of fusion [7], no specific classification for analyzing the prepared capsules was required. The scanning temperature range and the heating rate were -40～+400℃ and 5℃/min, respectively.

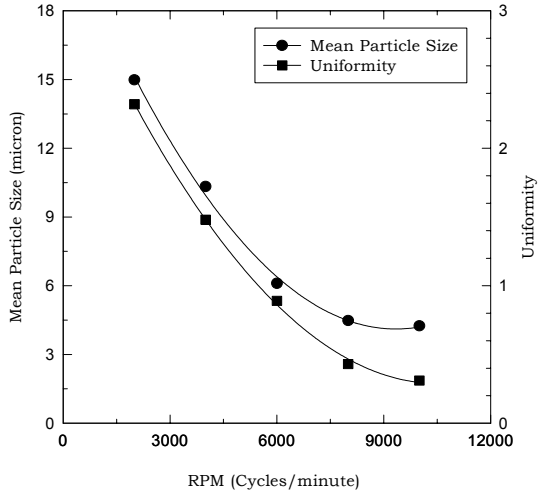

Fig. 1. Effect of rpm on particle size and uniformity of microcapsules prepared

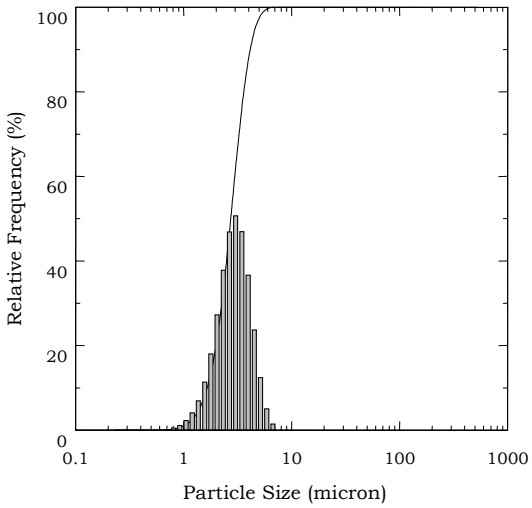

Fig. 2. Size distribution of the microcapsules containing various perfumes

Results and Discussion

The rpm of the homomixer in the emulsifying step was one of the important factors affecting both the size and the size distribution of the capsules. As shown in Figure 1, the mean particle size decreased and the uniformity of the capsules improved when the rpm of the homomixer was increased, indicating that the extent of homogenization was significantly affected by mechanical factors during emulsification. Therefore, the rpm of the equipment in the emulsifying step must be sufficiently high to obtain microcapsules with a high uniformity and desirable small size (generally, <50 μm). All following experiments were performed under the conditions where the rpm of the homomixer was up to 8000.

Figure 2 shows the results of the size distribution for the microcapsules containing fragrant oil as the core material. As shown in this figure, it was obvious that each product was comprised of particles with a normal frequency distribution within a narrow particle size range. The mean particle diameter of the capsules was estimated to be 5 μm within a range of 12 μm width.

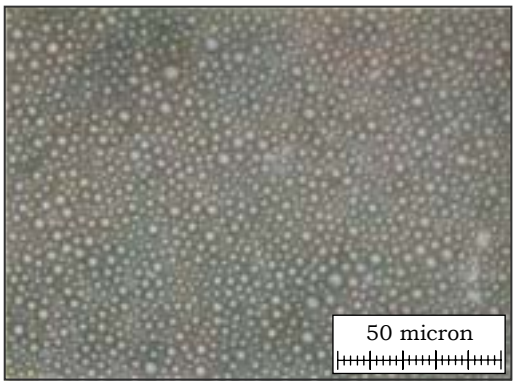

Fig. 3. Droplets investigated by the optical microscope in emulsifying step

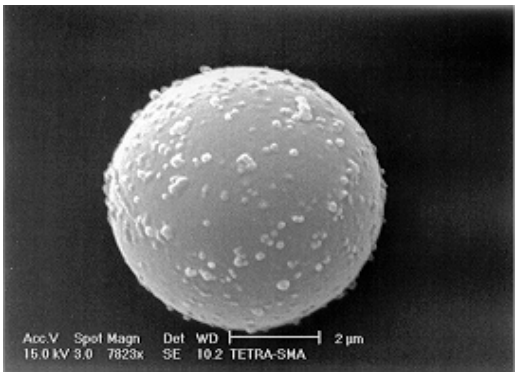

Fig. 4. SEM photograph of the capsule after polymerization step

The uniformity of the microcapsules is also demonstrated by Figure 3. This figure represents the shape, size, and size distribution of the droplets in the emulsifying step. Since uniform droplets lead to a final product comprised of microcapsules with good uniformity, it is very important that every aspect of the emulsifying step is carried out with careful attention [8, 9].

Figure 4 shows a scanning election photograph of a microcapsule containing fragrant oil as the core material surrounded by a melamine-formalin crosslinked shell.

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