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Preparation process of functional particles: II. Particle coating by rapid expansion of supercritical fluid solutions

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기능성 미분말의 제조공정에 관한 연구: II. 초임계 분출법에 의한 입자 코팅

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Abstract The Rapid Expansion of Supercritical fluid Solutions (RESS) process was applied to particles coating. Experiments were conducted in a fluidized bed with an internal nozzle in the center of the reaction tube. Pure glass beads (500~590 μm, 74~149 μm) and glass beads covered with brilliant blue were used as the core particles. Supercritical CO_2 solutions of paraffin were expanded through the nozzle into the bed that was fluidized by air. The precipitate coating materials on core surface was analyzed by using SEM, FT-IR. The releasing behavior of brilliant blue was inspected by atomic absorbance spectrophotometer. The release behavior of coated particles superior to noncoated particles.

요 약 초임계 분출법(RESS)을 미립자 코팅에 이용하였다. 본 실험은 반응관 중심부에 위치한 노즐을 갖고있는 유동층 내부에서 수행하였다. 핵입자로는 glass beads(500~590 μm, 74~149 μm)와 brilliant blue로 피복된 glass beads의 두 종류를 사용하였다. paraffin이 용해된 초임계 CO_2는 공기에 의해 유동중인 유동층 내부 노즐을 통해 분무시켰다. 핵입자 표면에 코팅물질이 피복됨을 SEM과 FT-IR에 의한 분석을 통하여 확인할 수 있었다. 코팅 전후 brilliant blue의 용출특성을 ABS로 조사한 결과 코팅입자의 용출특성이 향상되었음을 확인하였다.

1. Introduction

A large number of techniques exist for the production of thin film or fine powders for use in a variety of applications. All such techniques, however, have limitations, either in the types of materials for which they can be used, or in the physical form or chemical characteristics of the production. So a novel technique, which is so called the rapid expansion of supercritical fluids solutions (RESS), was developed for the production of fine powders and thin films from any material which can be dissolved in a supercritical solvent [1]. A supercritical fluid is broadly defined as a substance above its critical temperature and critical pressure, where it remains in a single fluid phase regardless of the applied pressure. Supercritical fluids are characterized by greatly enhanced solvent power compared to subcritical liquid, because press strongly affects supercritical fluid densities, which may approach those of liquids [1-5].

Recently, a new fluidized bed coating process was proposed in which supercritical fluid solutions of coating material were introduced into the bed. The RESS through short nozzle can be considered to be an adiabatic expansion. So pressure decreases extremely and solubility of coating materials increases highly. Then the solute (coating materials) can be precipitated on the surface of core particles in fluidizing [2].

2. Experimental procedures

In this study, the RESS process was applied to particle coating. The experimental apparatus is schematically shown in Fig. 1. It consist of an acryl vertical-tube reactor (1500 mm long, 50 mm ID and

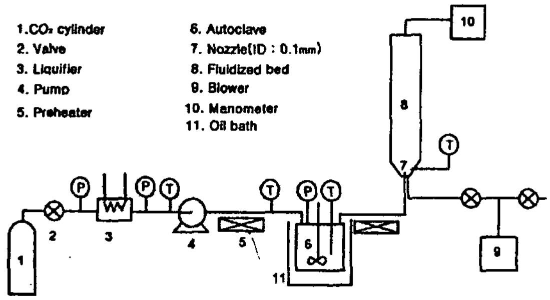

Fig. 1. Schematic experimental apparatus.

corn angle 60 degree), an autoclave (V: 0.001 m^3, max. pressure: 400 kg/cm^2, max. temperature: 300℃) with a stirrer, a high pressure pump, a carbon dioxide supply system, a blower, a liquefier and a pre-heater. A stainless steel nozzle (ID: 0.1 mm) was located at the center of the corn part.

Core particles are used two types of glass beads (particle size distribution: 500~590 μm and 74~149 μm, respectively) and glass beads covered with brilliant blue (Katayama Chemical., special grade) mechanically. Coating material was used paraffin that the melting point was 48~50℃. Core particles of 50 g were fluidized with air from blower in which air flow rate was 3~4 l/min. Liquefied carbon dioxide was delivered to the autoclave (100℃, 150 kg/cm^2) containing paraffin. To increase the solubility

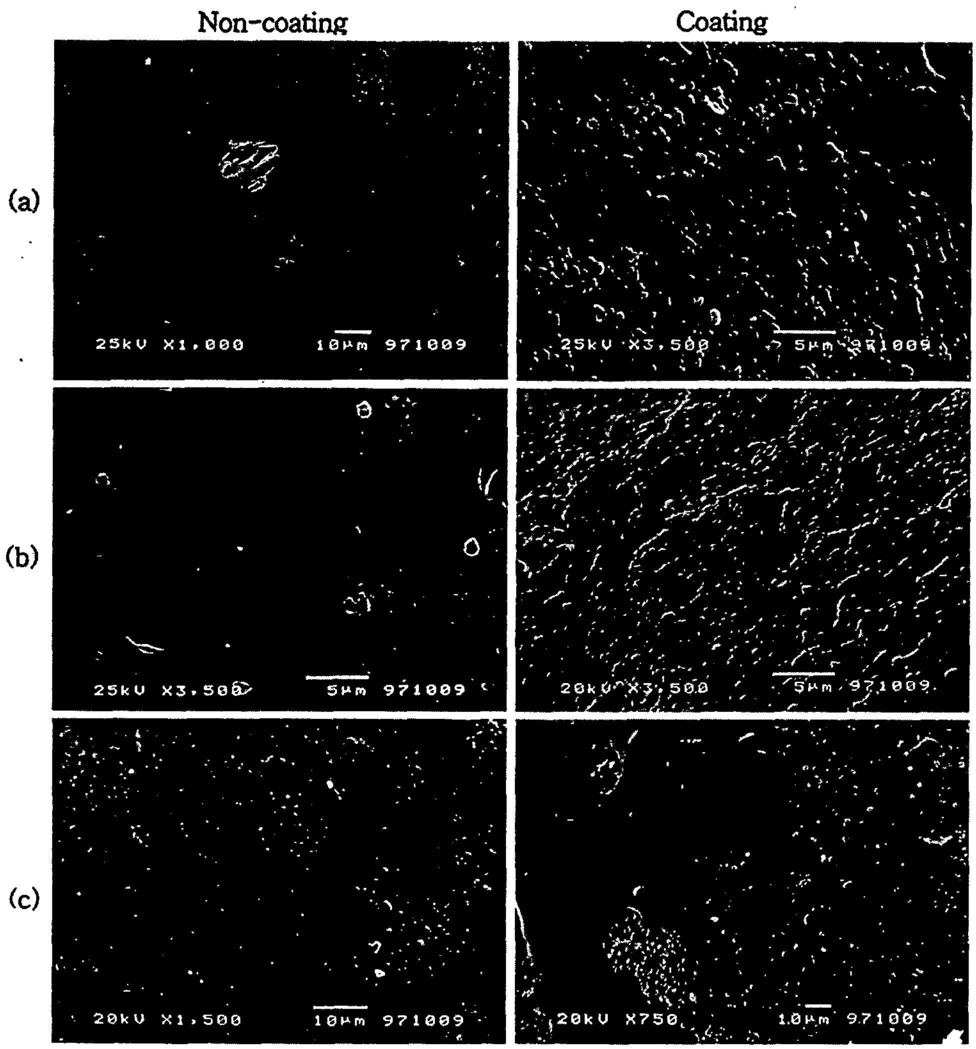

Fig. 2. SEM photographs of glass beads. (a) glass beads of 500~590 μm, (b) glass beads of 74~149 μm, (c) glass beads covered with brilliant blue.

of paraffin in supercritical CO_2, the autoclave was sustained above the critical point of paraffin. The supercritical carbon dioxide solution of paraffin was expanded into the reaction tube through the short nozzle. The nozzle was maintained at a temperature of 100℃ (above the paraffin melting point) by a line heater for the purpose of preventing the precipitation of paraffin. During expansion, supercritical CO_2 was fed into the reaction tube by the high-pressure pump at a constant flow rate. The flow rate of CO_2 was fixed at 7~8 *l*/min. The reaction time was also fixed at 90 min.

After the reaction, the coated particle was observed with scanning electron microscope (SEM, JMSL5410: Jeol, Ltd., Tokyo, Japan) In case of that particle size distribution is 500~590 μm and 74~149 μm, respectively, qualitative analysis the coated glass beads was performed by FT-IR ("Protebe460": Nicolet Instrument Corporation, Madison, USA). In the case of glass beads covered with brilliant blue, release behavior of brilliant blue with time in H_2O was measured using an atomic absorbance spectrophotometer (ABS, 100~50 type: Hitachi, Ltd., Tokoy, Japan)

3. Results and Discussion

Figure 2 shows the surface morphology of each particle using SEM. Coated particles show different morphologies from that of non-coated particle. The pure glass beads have a smooth morphology, but coated particles were observed anything adhered to the surface. From this result, the authors thought that adhered materials were paraffin. One can observe the existence of the paraffin coating layer. And in this figure, coating mass of glass beads of 74~149 μm (Fig. 1 (b)) was superior to that of glass beads of 500~590 μm (Fig. 1 (a)). This result accords with Abe et al. [6], who reported that the smaller particles, the better coating efficiency. So we thought that the fluidity of smaller particles was excellent in the reaction tube and the flighting distance became long.

To inspect whether the particle coating is complet or not, paticle surface before and after the coating process was investigated qualitative analysis using FT-IR. Figure 3 shows that result. As shows in this figure, peak shapes before and after the coating process were similar each other, but coated particles show C-H band of general saturated hydrogen carbide in the vicinity of 2484 cm^{-1} and 2920 cm^{-1}. This result proved that the paraffin coating on the core particle surface was complete. And the reason for C-H band peaks appeared a difference wave number was thought to be due to the effect of C-H band vibration mode.

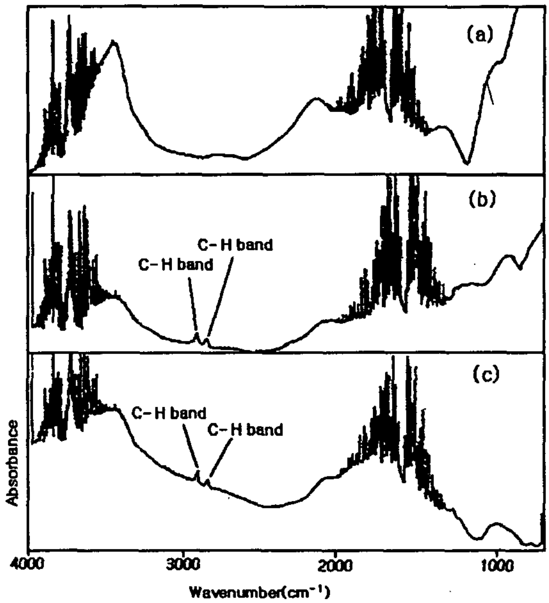

Fig. 3. Infrared spectra of glass beads. (a) non-coating glass beads (500~590 μm), (b) coating glass beads (500~590 μm), (c) coating glass beads (74~149 μm).

Figure 4 shows the result of release behavior of brilliant blue using atomic absorbance spectrophotometer. This figure noted the solubility with time, if the brilliant blue would be dissolved 100 % to total measuring time. From this figure, before and after the paraffin coating, the required time for brilliant blue to dissolve 100 % was 30 sec and about

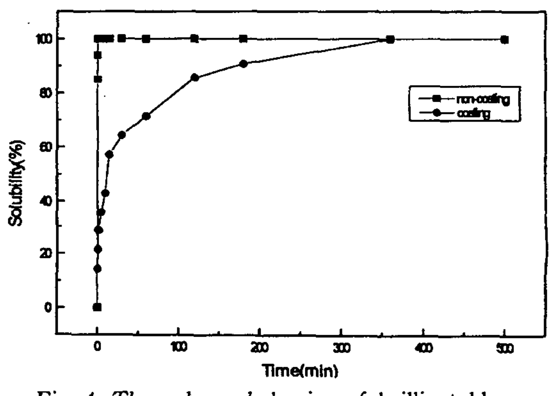

Fig. 4. The release behavior of brilliant blue.

6 hr, respectively. The release behavior of coated particles was superior to that of non-coated particles. From this result, it is considered indirectly that paraffin coating using RESS process was suceeded, and it was possible to control the releasing time.

4. Conclusions

Fine particles coating by the rapid expansion of supercritical CO_2 solutions of paraffin was performed in a fluidized bed with an internal nozzle at the center of the vertical tube. The coating process by the RESS allows not only particle coating, but also low temperature coating. And it is possible to be overdued releasing time by RESS coating process.

This suggests the possibility of wide application in industry, especially, pharmaceutical, processed food and fertilizer.

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