A PRODUCTION PROCESS FOR UNIFORM-SIZE POLYMER PARTICLES

SHIRO MATSUMOTO, KENJI TAKESHITA, JIRO KOGA
AND YOICHI TAKASHIMA

Department of Environmental Chemistry, Faculty of Engineering, Saitama University

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1. Introduction

Porous polymer particles are widely used as ion exchange resins or packing materials for chromatography. Uniformity of particle size is an important factor in reproducible separation performance. Therefore, great concern has been taken for the production of single-size polymer particles.

Generally, polymer particles are made by the process of suspension polymerization, in which fine droplets of monomer are suspended in a dispersion medium with a stabilizer like polyvinyl alcohol. However, agglomeration of the droplets or their

adhesion to the reactor wall is inevitable in this method,

because the viscosity of dispersed phase increases with the degree of polymerization.^{2,3)} It is, therefore, difficult to control particle size and produce single-size particles.

In the work described in this paper we have developed a new process for producing single-size polymer particles. The process consists of several steps, such as the formation of single-sized and concentric two-phase droplets, the solidification of the outer phase, the polymerization of monomer in the inner phase and the removal of shell material. A copolymer of styrene and divinylbenzene was produced by this process. The uniformity of particle size was much better than that by the conventional

* Received February 4, 1989. Correspondence concerning this article should be addressed to S. Matsumoto. K. Takeshita and Y. Takashima are at Institute of Research and Innovation.

suspension polymerization.

1. Process description and background

Figure 1 shows the process concept for producing single-size polymer particles. The first step is the formation of single-size and concentric two-phase droplets, in which the monomer is encapsulated with a solution of shell material. The droplets can be generated by using a dual and coaxial nozzle vibrated at the optimum frequency.^{4,5)}

Figure 2 shows a schematic diagram of experimental apparatus which was used previously for encapsulation.⁴⁾ A dual and coaxial nozzle, installed at the core of a speaker, is vibrated vertically. The monomer to be encapsulated is fed through the inner tube, while the solution of shell material is fed through the annulus space.

The mechanism of uniform droplet formation can be explained by Rayleigh's analysis for the instability of jet flow.⁶⁾ The droplets are generated by selecting the total flow rate of monomer and shell material, Q , and the frequency of vibration, f , which give maximum instability to the jet flow.⁴⁾ The drop diameter, d_p is given by

$$d_p = (6Q/\pi f)^{1/3} \quad (1)$$

and, for the diameter of inner phase, d_{in} ,

$$d_{in} = (6Q_{in}/\pi f)^{1/3} \quad (2)$$

where Q_{in} denotes the flow rate of monomer.

The second step is the stabilization of capsules by hardening the solution of shell material. It can be completed by coacervation, chemical reaction or drying, which should be selected according to the properties of the solution of shell material.

The third step is the polymerization of monomer in the capsule. The polymerization may be carried out by suspending the capsules in a stirred tank.

Finally, the polymer particles are obtained by removing the shell material from the capsule. This may be carried out by a chemical process, which should be selected according to the properties of the shell material.

2. Examination and Discussion

Two examinations were carried out for producing particles made of styrene-divinylbenzene copolymer. Styrene and divinylbenzene monomers containing 0.6wt% benzoyl peroxide as an initiator were prepared. The monomers were encapsulated with the shell material of 0.8wt% sodium alginate solution. The solution of shell material was hardened as calcium alginate in 20wt% CaCO_3 solution.

The capsules were suspended in a stirred tank at constant temperature of 75°C for seven hours. Neither agglomeration of the capsules nor adhesion to the

Fig. 1. Process concept for producing uniform-size polymer particles

Fig. 2. Schematic diagram of experimental apparatus for producing concentric two-phase droplets

1. N_2 cylinder	2. buffer tank
3. monomer reservoir	4. shell material reservoir
5. rotameter	6. orifice flow meter
7. dual axial nozzle	8. hardening agent
9. speaker	10. amplifier
11. oscillator	12. lamp
13. photo sensor	14. digital counter
15. oscilloscope	

Fig. 3. Copolymer of styrene and divinylbenzene of 2.3 mm diameter, produced by the conditions of $Q_{in} = 26.7$ ml/min, $Q_{out} = 41$ ml/min and $f = 70$ Hz. The inner and outer diameters of the nozzle are 0.75 mm ϕ and 1.2 mm ϕ , respectively.

reactor wall occurred during the polymerization. Therefore, it was not necessary to use a stabilizer as is done in conventional suspension polymerization. The polymer particles were obtained by removing the shell material from the capsules in 10 wt% sodium polyphosphonate solution. All procedures were accomplished in ten hours.

Typical photographs of the polymer particles are shown in **Figs. 3** and **4**. The mean diameters of polymer

Fig. 4. Copolymer of styrene and divinylbenzene of 500 μm diameter, produced by the conditions of $Q_{in}=0.79$ ml/min, $Q_{out}=1.1$ ml/min and $f=200$ Hz. The inner and outer diameters of the nozzle are 0.13 mm ϕ and 0.2 mm ϕ , respectively.

particles were 2.3 mm and 500 μm , respectively. The diameter can be controlled by adjusting the operating conditions such as the flow rate of monomer and the frequency of vibration. The uniformity of particle size was so excellent that the standard deviations were only about 2% for the particles of 2.3 mm diameter and about 8% for those of 500 μm diameter.

Conclusion

A new process has been proposed for producing single-size polymer particles. The uniformity of

particle size is much better than that by conventional polymerization processes. Particles of the arbitrary size selected can be produced by adjusting the flow rate of monomer and the frequency of vibration.

Nomenclature

d_p	= diameter of two-phase droplet	[m]
d_{in}	= diameter of inner phase	[m]
f	= frequency of vibration	[1/s]
Q_{in}	= flow rate of monomer	[m ³ /s]
Q_{out}	= flow rate of shell material	[m ³ /s]
Q	= total flow rate ($=Q_{in}+Q_{out}$)	[m ³ /s]

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