NOVEL PROCEDURE FOR MONODISPERSED POLYMERIC MICROSPHERES WITH HIGH ELECTRIFYING ADDITIVE CONTENT BY PARTICLE-SHRINKING METHOD VIA SPG MEMBRANE EMULSIFICATION

HIDEKAZU YOSHIZAWA, HIDEKI OHTA, MASA-AKI MARUTA,
YOSHIMITSU UEUMURA, KAZUYA JJICHI AND YASUO HATATE
Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Kagoshima University, Kagoshima 890

Keywords: Materials, Polymeric Microsphere, SPG Membrane Emulsifier, Suspension Polymerization, Toner Particles

Introduction

Monodispersed particles are widely used in industrial and pharmaceutical fields such as spacers for liquid crystalline display, toner particles, and dosage forms of drugs. In general, it is well known to be difficult to yield particles with narrow diameter distribution and great effort has been devoted to prepare monodispersed polymeric microspheres of 10 µm in diameter.

The SPG membrane emulsification technique is a promising one to yield monodispersed droplets continuously both in O/W emulsion and W/O emulsion systems (Nakashima and Shimizu, 1993). By applying this technique, polymeric microspheres of which diameter was ca. 10 µm have been successfully prepared by several research groups (Hatate et al., 1995; Omi et al., 1994). However, when viscous liquid or highly-concentrated solutions were used as a dispersed solution, the diameter distribution of dispersed droplets became broader and this resulted in a wide diameter distribution of polymeric microspheres after polymerization. So, we tried to prepare monodispersed droplets and polymeric microspheres containing high contents of additives by diluting with a volatile solvent with SPG membrane emulsifier at first and subsequently removing the solvent from the prepared emulsion.

In this article, the preparation of toner particles with high contents of electrifying additives was demonstrated as an adequate case of adopting this procedure.

1. Experimental

1.1 Materials

The monomer and crosslinker used in this study were styrene (St) and divinylbenzene (DVB), respectively, and these agents were distilled at reduced pressure before use to remove inhibitors. DVB was of 55% purity. These reagents were stored in a refrigerator prior to use. 2,2'-azobisisobutyronitrile (AIBN) and 2,2'-azobisis(2,4-dimethylvaleronitrile) (ADVN) were used without further purification. E-81 and SPBS were the charge control agent and coloring matter, respectively, and were used as received.

1.2 Preparation of polymeric microspheres by particle-shrinking method

The protocol for the preparation of polymeric microspheres used in this study is shown in Fig. 1. The particle shrinking method consists of three main processes: SPG membrane emulsification, solvent evaporation and suspension polymerization. The detailed conditions of the respective parts are as follows.

Table 1 represents the preparation recipe of O/W emulsion. The dispersed phase was monomer solution diluted with dichloromethane. Radical initiators and electrifying additives were dissolved in the dispersed phase. The continuous phase was an aqueous solution of PVA and SDS. In the SPG membrane emulsification process, POEM-LABO®, which was supplied from Reika Kogyo Co., Ltd., was used to prepare the O/W emulsion. The pore diameter of the SPG membrane in this study was 3 µm. It was supplied by The Ohtsu Tire & Rubber Co., Ltd.. The detailed procedure for the O/W emulsion preparation was the same as mentioned previously (Hatate et al., 1995).

After preparation of the O/W emulsion, it was charged into a ca. 0.8 dm³ separator flask with a two-blade, screw-type agitator and the solvent evaporation process was carried out at 303 K for 43.2 ks with a stirring of 1.67 s⁻¹. In this process, dichloromethane was removed and the dispersed droplets were shrunk until they were ca. 80% of the diameter predicted theoretically.

Subsequently, the suspension polymerization
was carried out at 328 K for 21.6 ks under an agitation rate of 2.5 s⁻¹. The prepared polymeric microspheres were washed with hot water to remove the adhesive polyvinyl alcohol and dried in vacuo at room temperature.

1.3 Characterization of polymeric microspheres
The average diameter and diameter distribution of polymeric microspheres and dispersed droplets were measured by an optical photographic method. The average diameter was number-averaged.

The morphology of the prepared polymeric microspheres coated with gold prior to examination was observed by scanning electron microscopy (JEOL JSM-840) at an intensity of 15.0 kV under various magnifications.

Figure 2 represents an optical microscopic photograph of dispersed droplets of the O/W emulsion where dispersed droplets were monomer solution diluted with dichloromethane. The content of SPBS was 4.0 wt% in dispersed droplets. From this figure, it was found that oil droplets were well dispersed and had fairly narrow diameter distribution. The average diameter of oil droplets was 10.4 μm, which was 3.47 times the pore diameter of the SPG membrane. Nakashima and Shimizu, and Omi et al. reported that the coefficients were 3.25 and 6.62, respectively. The variation of the coefficient may be due to the difference of the SPG membrane used (Omi et al., 1994).

Figure 3 illustrates the diameter change of the dispersed droplets and polymeric microspheres prepared by the procedure proposed in this study. As can be seen in this figure, the average diameter of particles gradually became smaller due to the removal of dichloromethane at the solvent evaporation step, and the density difference between monomer and polymer at the suspension polymerization step. The shrinking percentage of dispersed droplets after the solvent evaporation step was 89%, and this value implied that complete removal of dichloromethane from the dispersed droplets was not attained yet. It may be considered that removal of dichloromethane continued in the succeeding step. The average diameter of polymeric microspheres finally obtained was 73% of that of the dispersed droplets in O/W emulsion just after the SPG membrane emulsification step. The resulting shrinking ratio was reasonable, considering the fraction of dichloromethane in the initial dispersed solution and the density difference between styrene and polystyrene.
An SEM photography and diameter distribution of the obtained polymeric microspheres, having higher content of SPBS, are shown in Fig. 4. The prepared polymeric microspheres are spherical and monodispersed polymeric microspheres can be yielded, though the diameter distribution of an O/W emulsion prepared by SPG membrane emulsification of higher viscous dispersed liquids or solutions of higher solute dispersed concentration was inclined to be much wide-spread. The electrostatic capacity of polymeric microspheres with 8.0 wt% of SPBS was measured by the previously mentioned manner and was found to be $-24.8 \mu C \cdot g^{-1}$ (Hatate et al., 1990).

**Conclusion**

Relatively uniform polymeric microspheres with electrifying additives of high concentration were prepared by combining SPG membrane emulsification with a solvent evaporation process. This procedure will be also applied to the SPG emulsification of viscous dispersed solution.

**Acknowledgment**

The authors wish to express their thanks to Mr. Tohru Taniguchi of Reika Kogyo Co., Ltd., Miyazaki, Japan, for supplying the SPG membrane emulsifier, POEM-LABO®. We also acknowledge Mr. Kazuma Kanaoka, of The Ohtsu Tire & Rubber Co., Ltd., Osaka, Japan, for supplying SPG membranes.

**Nomenclature**

- C.V. = coefficient of variation defined by $\sigma_d / \bar{d} \times 100$ or $\sigma_{d_p} / d_p \times 100$ [%]
- $d_d$ = diameter of dispersed droplets in emulsion [μm]
- $d_p$ = diameter of polymeric microspheres [μm]
- X = initial content of additives in dispersed phase (Fig. 1) [%]
- $\sigma$ = standard deviation of diameter distribution [μm]
- over bar = average value

**Literature Cited**


