Preparation of Monodispersed Polymeric Microspheres for Toner Particles by the Shirasu Porous Glass Membrane Emulsification Technique

YASUO HATATE, HIDEKI OHTA, YOSHIMITSU UEMURA, KAZUYA IJICHI, HIDEKAZU YOSHIZAWA*

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890, Japan

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ABSTRACT: This investigation describes the experiment directed toward the production of monodispersed toner particles by suspension polymerization. That is, relatively monodispersed poly(styrene-*co*-divinylbenzene) microspheres containing electrifying additives were successfully prepared by suspension polymerization employing the Shirasu Porous Glass (SPG) membrane emulsification technique. The diameter distribution of the dispersed droplets prepared with an SPG membrane module was fairly narrow, compared with that prepared with a conventional mechanical homogenizer. The effect of Sumiplast Blue S as coloring matter and E-81 as charge control agent on the triboelectric discharging properties of prepared polymeric microspheres was studied. The addition of electrifying additives strongly affected the triboelectric discharging property. It was consequently clarified that a small amount of electrifying additives added raised the electrostatic capacity of polymeric microspheres. However, a further addition reduced the triboelectric discharge of polymeric microspheres. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1107–1113, 1997

Key words: polymeric microsphere; monodispersion; SPG membrane emulsifier; suspension polymerization; electrostatic capacity

INTRODUCTION

The preparation of monodispersed polymeric microspheres having a 10-μm diameter has come to the attention of polymer researchers because the demand for these polymeric microspheres has been increased in diverse areas. Polymeric microspheres of 10-μm diameter with a narrow size distribution can be applied to fixed phases in liquid chromatography, enzyme-immobilized beads, electrophotographic toner particles, and so on. However, limited investigations have been proposed on the preparation procedure of monodispersed polymeric microspheres with 10-μm diameter. That is, only the following processes have been reported: seeded emulsion polymerization,[1] polymerization of monomer-swelled particles,[2,3] and conventional nonaqueous dispersion polymerization.[4] These processes are very complicated and require a long production time, although they promise the preparation of fairly monodispersed polymeric microspheres. Considering conventional suspension polymerization, which was widely adopted as a production process for commercially available polymeric microspheres, the problem of low yield and high cost is unavoidable because severe classification is necessary to prepare 10-μm diameter polymeric microspheres.

In addition to monodispersity, triboelectric discharging property is vital for toner particles in

Correspondence to: Hidekazu Yoshizawa.
* *Present address:* Dept. of Applied Chem. & Chemical Engr., Kagoshima University, 1-21-40 Korimoto, Kagoshima 890, Japan.
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electrophotography.[5] Furthermore, electrostatic capacity, one of the triboelectric discharging properties, was a function of the toner diameter. Nevertheless, fundamental studies on the production of monodispersed toner particles and the effect of diameter distribution on triboelectric discharging properties have been left for future work. In our previous articles, 100-μm polymeric microspheres with/without electrifying additives were prepared as model toner particles by conventional suspension polymerization, and their triboelectric discharging properties were reported.[6,7]

Considering this background of polymeric microspheres for toner particles, we adopted the SPG membrane emulsification technique to provide fairly uniformly dispersed droplets.[8] This emulsification process was developed by Nakashima et al. and is now utilized in the productions of margarine and the spacer in liquid crystalline display, and so on.[9–11]

This article describes the preparation and the triboelectric discharging property of fairly monodispersed polystyrene microspheres crosslinked with divinylbenzene by suspension polymerization via the SPG membrane emulsification technique. The objective of this study is to establish the synthesis procedure for the polymeric microspheres containing styrene-soluble electrifying additives with narrow diameter distribution and to clarify the effect of the electrifying additives, such as coloring matter and charge control agent, on the electrostatic properties.

EXPERIMENTAL

Materials

Styrene and divinylbenzene were used as monomer and crosslinking agent, respectively, after distillation at reduced pressure under a nitrogen atmosphere. Prior to use, these reagents were stored in a refrigerator. In this study, two polymerization initiators, 2,2′-azobis(isobutyronitrile) (AIBN) and 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN), were used as received.

The charge control agent and the coloring matter, which were soluble in the dispersed phase, were E-81 from Orient Chemical Industries Ltd. and Sumiplast Blue S (SPBS) from Sumitomo Chemical Co., Ltd., respectively.

Polyvinyl alcohol (PVA) from Wako Pure Chemical Industries, Ltd. was used as a suspension stabilizer. Sodium dodecyl sulfate (SDS) was reagent grade and used without further purification.

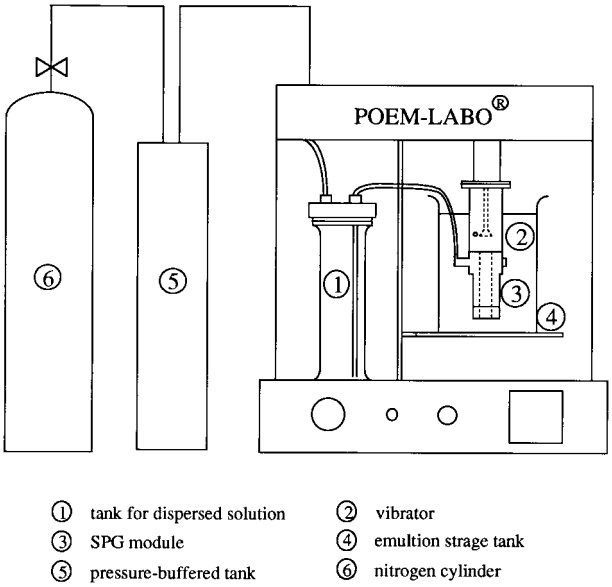

Figure 1 Schematic diagram of SPG membrane emulsifier used in this study.

Preparation of O/W Emulsion by the SPG Membrane Emulsification Technique

The SPG membrane emulsifier, POEM-LABO(R), which was supplied by Reika Kogyo Co., Ltd. was adopted to prepare the O/W emulsion. The schematic drawing of POEM-LABO(R) is illustrated in Figure 1. The preparation procedure of O/W emulsion with SPG membrane emulsifier used in this study was different from that used by Omi et al. with regard to the flow of the continuous solution.[12,13] In the SPG membrane emulsifier by Omi et al., the continuous solution axially flowed in a hollow-cylindrical SPG membrane; however, in this work, we operated the continuous solution batchwise, and the vibration was given to stir the solution in an emulsion storage tank. The SPG membrane with a pore diameter of 1.00, 2.00, and 3.00 μm was supplied by The Ohtsu Tire & Rubber Co., Ltd.

The preparation condition of the O/W emulsion is listed in Table I. The dispersed phase was a monomer solution containing polymerization initiators with/without electrifying additives. The continuous phase was an aqueous solution of PVA and SDS.

After the attachment of an SPG membrane with pores pre-filled with continuous solution by

Table I Recipe for Preparation of Polymeric Microspheres

Continuous phase	
PVA	1.0 wt %
SDS	0.1 wt %
Dispersed phase	
DVB/St	0.03 wt/wt
ADVN	0.1 mol·dm^{-3}
AIVN	0.1 mol·dm^{-3}
E-81	0–3.0 wt %
SPBS	0–3.0 wt %
Holdup of dispersed phase	5 vol %

ultrasonification, the dispersed solution was permeated through an SPG membrane, under the appropriate pressure, from the tank of the dispersed solution into the continuous solution. Thus, the solution in the emulsion storage tank has become opaque due to a gradual increase in droplet concentration. The detailed procedure for the operation of the SPG membrane emulsifier was described in the previous paper.[8] The SPG membrane was easily utilized many times by the regeneration process previously described.[8]

Suspension Polymerization

The apparatus for the preparation of polystyrene microspheres was a 0.8 dm^3 separator flask with a two-blade, screw-type agitator. The O/W emulsion prepared with an SPG membrane emulsifier was poured into the vessel, and the suspension polymerization was carried out for 21.6 ks at 328 K under a nitrogen atmosphere. In suspension polymerization, the agitator was operated at 2.5 s^{-1}. The prepared polymeric microspheres were washed with hot water to remove the adhesive polyvinyl alcohol and were dried in a vacuum at room temperature.

Average Diameter and Diameter Distribution

The average diameter and diameter distribution of the dispersed droplets in an O/W emulsion and the polymeric microspheres were measured by laser diffractometry using a COULTER(R) LS-130 (Coulter Electronics Co.). In some experiments, the average diameter measured by laser diffractometry was confirmed by comparison with one using scanning microscopic observation. The average diameter mentioned in this investigation was number-averaged.

Morphological Observation

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

Triboelectric Charge Measurement

Polymeric microspheres subjected to triboelectric discharge measurement were prepared by rolling with spherical ferrite powders in a ball mill. The diameter of spherical ferrite powders was 600 μm. The preparation conditions of the triboelectric samples and the operational conditions of the blow-off equipment were previously described.[6]

RESULTS AND DISCUSSION

Preparation of O/W Emulsion Having 8-μm Dispersed Droplets

In the emulsification with the SPG membrane, the diameter of the dispersed droplets was well known to be a function of the pore diameter of the SPG membrane. Figure 2 represents the relationship between the average diameter of the dispersed droplets and the pore diameter of the SPG membrane. In this experiment, the dispersed so-

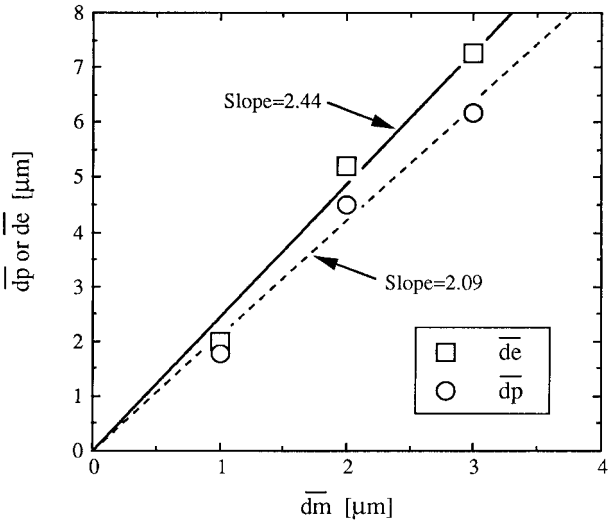

Figure 2 Plots of average diameters of dispersed droplets or polymeric microspheres against pore diameter of SPG membrane.

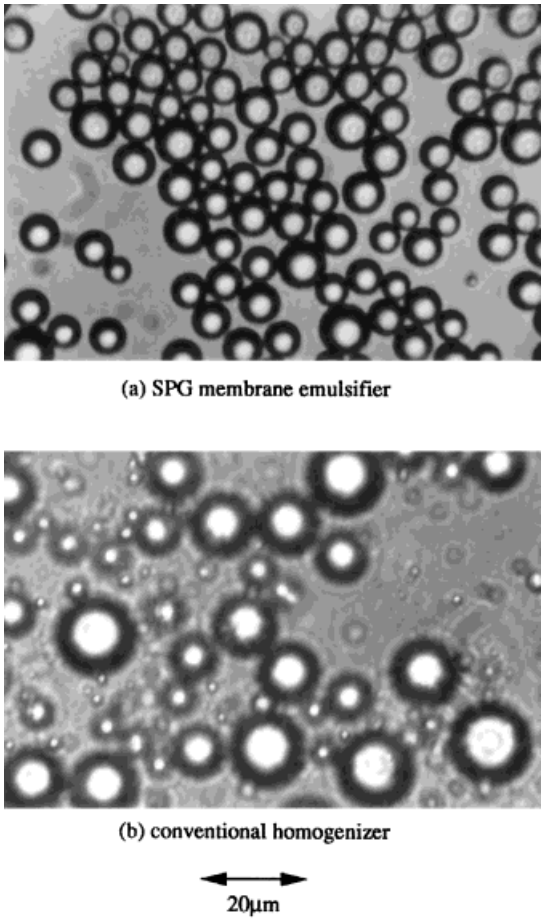

Figure 3 Optical photographs of dispersed droplets prepared by SPG membrane emulsification technique (a) and conventional homogenization (b).

lution was a mixture of St and DVB containing polymerization initiators, and the continuous solution was an aqueous PVA solution of SDS. As can be seen in this figure, the average diameter of the dispersed droplets (d_e) was $\sim$ 2.4 times larger than the pore diameter of the SPG membrane (d_m), and the following relationship was obtained.

$$d_e = 2.44 \times d_m$$

In this study, the proportional constant we obtained was 2.44; however, in their studies, Nakashima et al. and Omi et al. proposed that the constants were 3.25 and 6.62, respectively. The difference in the proportional constant may be due to the difference in the geometrical shape at the opening of the micropores, as described by Omi et al.[12,14] Because toner particles used in diverse fields are $\sim$ 8 μm in diameter, the SPG membrane with a 3.0-μm pore diameter was mainly used in the subsequent investigation.

The optical photograph of the dispersed droplets by the SPG membrane emulsification technique is illustrated in Figure 3. The result with a homogenizer is also shown in this figure. By comparing these two photographs, it was clear that the dispersed droplets prepared by the SPG membrane technique were fairly monodispersed.

Triboelectric Discharge of Polymeric Microspheres

Polymeric Microspheres without any Electrifying Additive

The O/W emulsions shown in Figure 3(a) were poured into the reactor, and the suspension polymerization progressed under a nitrogen atmosphere to obtain monodispersed polymeric microspheres. The average diameters of the polymeric microspheres were plotted against the pore diameter of the SPG membrane used in Figure 2. As a result, the following equation was obtained between the average diameter of the polymeric microspheres and the pore diameter of the SPG membrane.

$$d_p = 2.09 \times d_m$$

As shown in this figure, after polymerization, the average diameter became smaller and was 86% of the one before polymerization.[12]

Figure 4 represents the diameter distribution of polymeric microspheres prepared by the polymerization of monodispersed O/W emulsion via the SPG membrane emulsification technique, where an SPG membrane with a 3.0-μm pore diameter is employed. As can be seen in this figure, it is clear that the monodispersion was maintained after polymerization, and polymeric microspheres having a narrow diameter distribution were obtained.

To investigate the triboelectric discharging

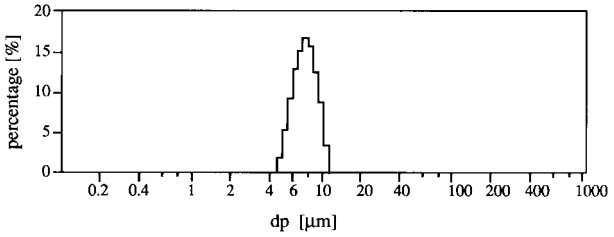

Figure 4 Diameter distribution of polymeric microspheres by SPG emulsification technique.

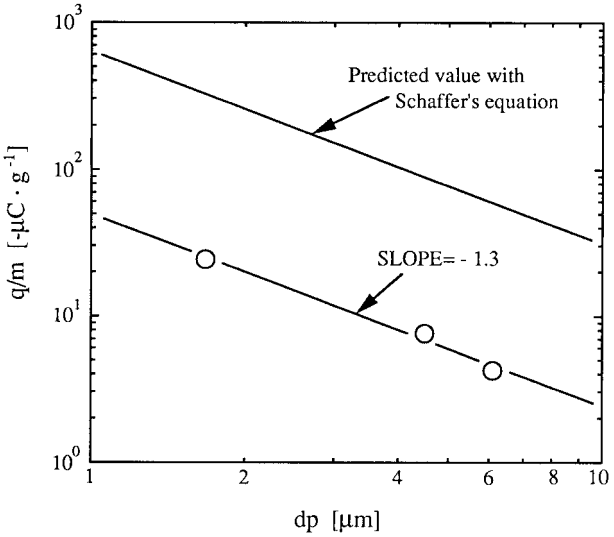

Figure 5 Effect of diameter of polymeric microspheres on electrostatic capacity; solid line represents the calculated value of electrostatic capacity with Schaffer's equation.

property of polymeric microspheres prepared by the SPG emulsification technique, Figure 5 shows the effect of the average diameter of the polymeric microspheres on electrostatic capacity. It was clearly indicated that the electrostatic capacity of polymeric microspheres decreased with an increase in the average diameter, and that the dependency of the electrostatic capacity on the average diameter was -1.3 power. This dependence on particle diameter shown in Figure 5 is almost the same as those in Schaffer's equation[15] and our previous study.[6] However, the electrostatic capacity was smaller than that predicted from Schaffer's equation with 1.04 $g \cdot cm^{-3}$ of polystyrene density. This may be attributed to the PVA used as the dispersion stabilizer in suspension polymerization. Because all the PVA molecules adhering on the polymeric microsphere surface cannot be removed by washing with hot water; several hydrophobic parts of PVA were buried in the polymeric microspheres. In this study, the measurement of the triboelectric discharging property was carried out several times, and the data of the electrostatic capacity were confirmed to be reproducible. Although calcium phosphate was also used as a dispersion stabilizer, it was difficult at the present stage to prepare an emulsion containing solid particles in the SPG membrane emulsification technique because of a blockage of the pores in the SPG membrane.

Polymeric Microspheres with Electrifying Additives

Toner particles contain various additives such as a coloring matter and a charge control agent. These additive matters have been well known to strongly influence the triboelectric discharging properties. In this study, SPBS and E-81 were chosen as coloring matter and charge control agent, respectively, and the effect of the additive matter content on the electrostatic capacity was investigated.

Representative SEM photographs of polymeric microspheres containing electrifying additives are shown in Figure 6. While the addition of SPBS and E-81 into the dispersed solution led to the higher permeation pressure in the SPG membrane emulsification, the polymeric microspheres prepared under a wide range of the electrifying additive content were fairly monodispersed, and the agglomeration of the dispersed droplets was not observed, as shown in Figure 6.

Figure 7 illustrates the effect of the coloring matter content (SPBS) on the electrostatic capacity of polymeric microspheres containing 1.0 wt % of E-81 as a charge control agent. The broken line represents the data of the polymeric microsphere without electrifying additives. It can be seen in Figure 7 that the electrostatic capacity increased as the SPBS content increased at up to 1.5 wt % of the SPBS content and that the maximum value was obtained at 1.5 wt %. However, the further addition of SPBS was found to reduce the electrostatic capacity. As stated in our previous study for the triboelectric discharge of polymeric microspheres having 100-μm diameter, this reduction

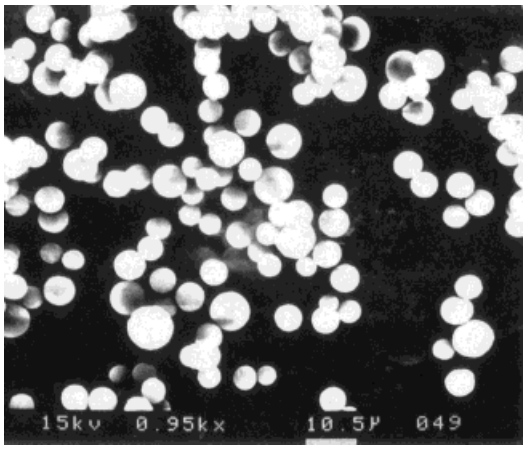

Figure 6 SEM observation of polymeric microspheres containing electrifying additives by SPG membrane emulsification technique.

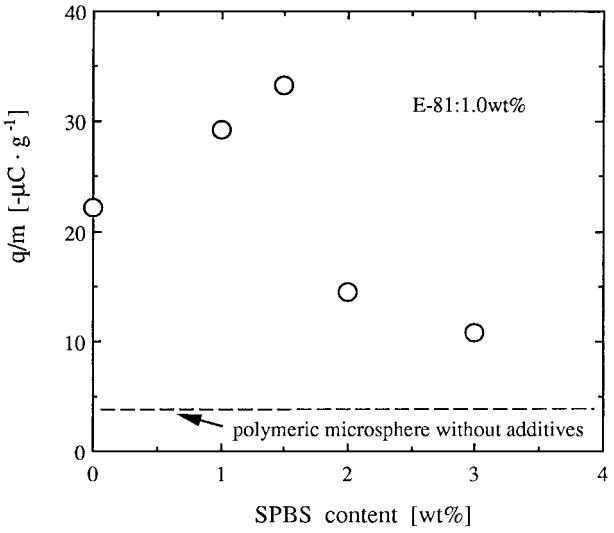

Figure 7 Effect of coloring matter content in polymeric microspheres on electrostatic capacity.

of the electrostatic capacity is probably due to the isolation disintegration of static electricity.[7] That is, the high content of SPBS in a polymeric microsphere leads the high contribution of formation of the electric circuit in/on polymeric microspheres to obtain a low electrostatic capacity because SPBS is a good electric conductor.

Figure 8 represents the effect of the charge control agent E-81 on the electrostatic capacity. All of the polymeric microspheres used contained 1.0 wt % SPBS. The maximum value of the electrostatic capacity of $-37.7\ \mu C \cdot g^{-1}$ was achieved at the E-81 content of 0.5 wt %. The dependency of the electrostatic capacity on the content of the charge control agent was fairly similar to that of the coloring matter content shown in Figure 7. That is, a small amount of added charge control agent increased the electrostatic capacity of the polymeric microspheres; however, an addition of the charge control agent above the adequate content resulted in a decrease in electrostatic capacity.

CONCLUSIONS

The SPG membrane emulsification technique was applied to prepare relatively uniform polymeric microspheres with/without electrifying additives for toner application. Using styrene-soluble electrifying additives, their effects on the triboelectric discharging property were investigated.

The following results were obtained:

1. The SPG membrane emulsification technique can provide fairly monodispersed droplets in O/W emulsion under a wide range of relevant conditions, such as the pore diameter of the SPG membrane and the content of the electrifying additives. Furthermore, being monodispersed, their diameter distributions were retained after suspension polymerization.
2. The electrostatic capacities of polymeric microspheres by the SPG membrane emulsification technique were smaller than those predicted by Schaffer's equation. This result reflected the use of polyvinyl alcohol as a dispersion stabilizer. Solid particles such as calcium phosphate will be preferred to increase the electrostatic capacity.
3. The effects of electrifying additives were significant. The appropriate additions of electrifying additives would result in an increase in electrostatic capacity.

LIST OF SYMBOLS

d_e = diameter of dispersed droplets in emulsion
d_m = pore diameter of a SPG membrane
d_p = diameter of polymeric microspheres
m = sample weight
q = electrostatic capacity
over bar = average value

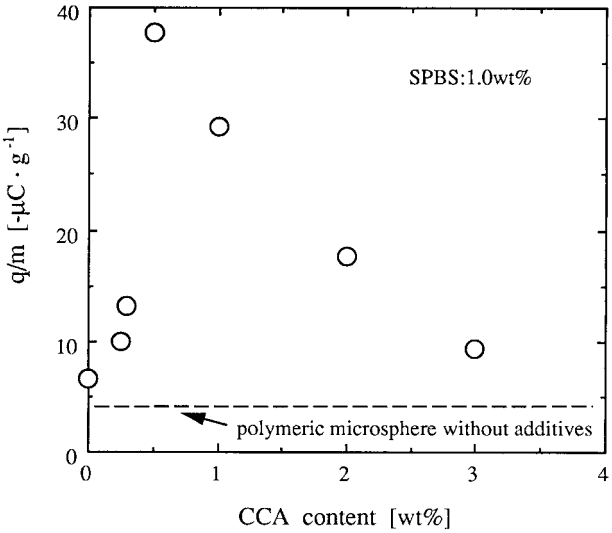

Figure 8 Effect of charge control agent in polymeric microspheres on electrostatic capacity.

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