ELECTROSTATIC PROPERTIES OF POLY (STYRENE-CO-DIVINYLBENZENE) MICROSPHERES WITH DIFFERENT SURFACE MORPHOLOGIES

YASUO HATATE, SHIN'ICHI HIGO, YOSHIMITSU UEMURA, KAZUYA IJICHI AND HIDEKAZU YOSHIKAWA

Department of Applied Chemistry and Chemical Engineering, Kagoshima University, Kagoshima 890

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Introduction

Much attention has been devoted to polymeric microspheres as advanced materials in diverse areas. Various procedures to synthesize polymeric microspheres have been investigated. The preparation procedures, especially suspension polymerization, are convenient for toner applications because it is easy to introduce additional functions^{1, 2, 3)}.

One of the most important aspects of toner is its triboelectric property, i.e., electrostatic capacity. It is considered that the charged area is localized in the vicinity of the surface rather than in the bulk⁴⁾. However, triboelectric phenomena are so complicated that many aspects of triboelectric mechanisms have been left for future works.

In this study, poly (styrene-co-divinylbenzene) microspheres (hereafter called poly (St-co-DVB) microspheres) that have different types of surface morphology were prepared by suspension polymerization in the presence of various types of diluents. The effect of geometrical shape of surface morphology on electrostatic properties was investigated using these polymeric microspheres.

1. Experimental

1.1 Materials

St and DVB used in this work were of reagent grade. These monomers, containing the inhibitor *t*-Butyl hydroxy toluene, were purified by distillation at reduced pressure under a N₂ atmosphere. The initiator for radical polymerization was lauryl peroxide (LPO). Calcium phosphate kindly supplied from Taihei Kagaku Co., Ltd. was adopted as a suspension stabilizer and was prepared by a precipitation method mentioned previously^{1, 2)}. The other chemicals were of reagent grade and were used without further purification.

1.2 Preparation of polystyrene microsphere

The apparatus for the preparation of poly (St-co-DVB) microspheres was a ca 0.8dm³ separable flask with a two-blade, screw-type agitator.

The dispersed phase consisted of St, DVB, LPO and a diluent such as toluene, *n*-dodecane or their equi-

volume mixture. The continuous phase was 0.005 wt% aqueous sodium *n*-dodecylbenzene sulfonate (DBSNa) solution containing 1.0 wt% calcium phosphate. Emulsification was carried out using homogenizer with an agitation rate of 21.7 s⁻¹. The O/W emulsion was then transferred to the polymerization apparatus. The polymerization temperature was 348 K. After polymerization, acetone washing and acid washing were repeated several times. The filtrated microspheres were dried in-vacuo and sieved to obtain the desired fraction (106 μ m to 125 μ m).

1.3 Characterization of microspheres

The morphology of the microspheres was observed by scanning electron microscopy (JEOL JSM-840) at an intensity of 15.0 kV under various magnifications.

Surface area and pore size distribution of the microspheres were measured with a porosimeter (Porosimeter 2000, CARLO ERBA).

Microspheres to be used in electrostatic capacity measurements were prepared by rolling in a ball mill with spherical ferrite powder 600 μ m in diameter. Preparation conditions for triboelectric samples and operation conditions for blow-off equipment were mentioned previously^{1, 2)}.

2. Results and Discussion

2.1 Characterization of microspheres

Representative results of SEM observations are illustrated in **Fig. 1** which shows the effects of diluents in the dispersed phase on surface morphology. Figure 1(a) shows a SEM photograph of a poly (St-co-DVB) microsphere without diluent. It was observed from this photograph that the surface of the microsphere was smooth. No pores were observed. Figs. 1(b) and 1(c) show surfaces of microspheres prepared with 40 vol% monomer and 60 vol% diluent (toluene and *n*-dodecane), respectively, in the dispersed phase. Toluene was used as a good solvent for polystyrene and *n*-dodecane was used as a poor solvent for polystyrene. A not so remarkable change was observed between Figs. 1(a) and 1(b). Conversely, microspheres prepared using *n*-dodecane show microporous structure (Fig. 1(c)).

Table 1 illustrates the effect of diluent on average

* Received March 3, 1994. Correspondence concerning this article should be addressed to H. Yoshizawa.

Table 1. Pore size distribution and bulk density of poly (St-co-DVB) microspheres made with 60 vol% diluent

Diluent	Total Pore Volume [cm ³ ·g ⁻¹]	Total Surface Area [m ² ·g ⁻¹]	Average Pore Radius [10 ⁻⁸ cm]	Bulk Density [g·cm ⁻³]
Toluene	0.0693	17.4	79.7	0.58
Toluene + <i>n</i> -Dodecane	0.0800	12.9	124.3	0.51
<i>n</i> -Dodecane	0.152	0.364	8337	0.22

(a) 100 vol% monomer, no diluent

(b) 40 vol% monomer, 60% toluene

(c) 40 vol% monomer, 60% *n*-dodecane

1 μm

Fig. 1 SEM photograph of poly (St-co-DVB) microspheres with/without diluent

pore diameter and bulk density of microspheres with 60 vol% diluent in the dispersed phase. Pore size distribution is shown in **Fig. 2**. The average pore size of microspheres in *n*-dodecane was about 100 times larger than that of microspheres in toluene. Pores having a diameter below 5 nm are observed for microspheres made with 60 vol% toluene. On the other hand, microspheres made with 60 vol% *n*-dodecane have pores around 1 μm in diameter. However, pore sizes are distributed between 5 nm and a

Fig. 2 Pore size distribution of poly (St-co-DVB) microspheres with diluent

Fig. 3 Effect of diluent on electrostatic capacity per unit weight of poly (St-co-DVB) microspheres

few μm in microspheres made with a toluene/*n*-dodecane mixture diluent. It is evident from Table 1 that microspheres made with *n*-dodecane have smaller bulk densities than those with toluene because the diameters of microspheres are more uniform after sieving. The differences in average pore diameter and the pore size distribution is considered to result in the difference in bulk density of the microspheres. Moreover, the outer surface area per microsphere can be varied by changing the diluent used in polymerization.

2.2 Electrostatic characterization of microspheres

Figure 3 shows the effect of monomer fraction in the dispersed phase, Φ , on the electrostatic capacity per unit mass, q/m . It was found from this figure that the value of q/m decreased with increasing monomer fraction in the

Fig. 4 Effect of diluent on electrostatic capacity per unit volume of poly (St-co-DVB) microspheres

dispersed phase when toluene and a toluene/*n*-dodecane mixture were used as the diluent. On the other hand, higher values of q/m were achieved at higher Φ for microspheres when *n*-dodecane was used as the diluent. That is, a different relation between q/m and Φ is obtained when a different diluent is used. The conflicting dependence of q/m on Φ mentioned above was considered to result from the difference in bulk density of the microspheres.

Figure 4 shows the relation between electrostatic capacity per unit volume, q/v and Φ . The value of q/v was calculated from q/m and the bulk density of the microspheres. It can be concluded from this figure that the electrostatic capacity per unit volume is well correlated only with Φ regardless of the choice of diluent and the fact that q/v decreases with increasing Φ . As microspheres prepared under conditions of larger Φ were thought to have smaller

outer surface area per microsphere, this result indicates that only the surface area subject to friction is a significant parameter in determining the triboelectric property of microspheres.

Conclusion

The effect of surface morphology on electrostatic capacity was investigated using polymeric microspheres prepared with toluene, a toluene/*n*-dodecane mixture and *n*-dodecane as diluent. The following conclusions were made.

Surface morphology can be changed by using diluents with different solubility parameters. The electrostatic capacity was, however, determined only by the void fraction of the microspheres, regardless of diluent. That is, it was found that the outer surface area able to contact with ferrite particles was the predominant factor in determining the triboelectric property of microspheres.

Nomenclature

m	= sample weight	[g]
q	= electrostatic capacity	[μC]
r_p	= pore radius	[cm]
v	= sample volume	[cm ³]
v_p	= pore volume	[cm ³ ·g ⁻¹]
Φ	= volume fraction of monomer	[-]

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