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Preparation of inorganic/polymeric composite microspheres by direct suspension polymerization

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Spherical polystyrene powders coated uniformly by γ-Fe_2O_3 or RuO_2 were obtained by means of a direct suspension polymerization. Starting reactant mixture was a complex disperse system comprising a fine powdered material, droplets of styrene monomer containing lauroyl peroxide as an initiator, and an aqueous medium. By varying the ratio between monomer and water, amount of powders as well as of the initiator, factors dominating particle size, volume fraction of fine powders adhered and the degree of polymerization were elucidated

1. Introduction

Promoted by increasing interests of developing functional polymers, various attempts have been made to prepare polymeric materials with high electrical conductivity, ferroelectricity or ferromagnetic properties. In most of the conventional methods, a simple mixing or kneading technique is used for those purposes. As a result, the dispersity of fine particles in the entire composite is not always satisfactory. This often leads to an unnecessarily high amount of loading, higher cost and, in many cases, lower mechanical quality.

To improve the shortcomings mentioned above, progress was made recently in obtaining microspheres containing functional powders in the core of each particle [1, 2]. Such microcapsules are not suitable, however, as far as a composite material with high electrical conductivity of ferroelectricity is concerned, since, in such cases, contiguity of the functional particles plays an important role. Instead, particles covered with a functional powdery material are much more desirable, because of the rational network formation with a minimum amount of loading as a result of an ordered mixing [3]. For the purpose of obtaining such coated particles, a simple mixing method was usually used [4]. Here again the problem of a poor dispersion on the surface of the host polymer particles was unavoidable. Exceptions would be an *in situ* reduction of metal-containing solution where polymeric powders are dispersed [5] and a metal-coating technique [6]. These are restricted, however, to several metallic materials.

The purpose of the present study is to prepare a composite material where a spherical polymer particle serves as a core, being coated by much smaller particles with high electrical conductivity or other functions. These are not only useful in allowing contiguity of the functional powders, but also as an unconsolidated free powdery material, e.g. for electrostatic painting or xerography.

2. Experimental techniques

2.1. The sample

Commercial styrene monomer was purified by washing with a dilute NaOH aqueous solution and distilled under reduced pressure. Photomicrographs of the powders, γ-Fe_2O_3 and RuO_2 (kindly donated by Toda Kogyo and Tanaka-Matthey) are shown in Fig. 1.

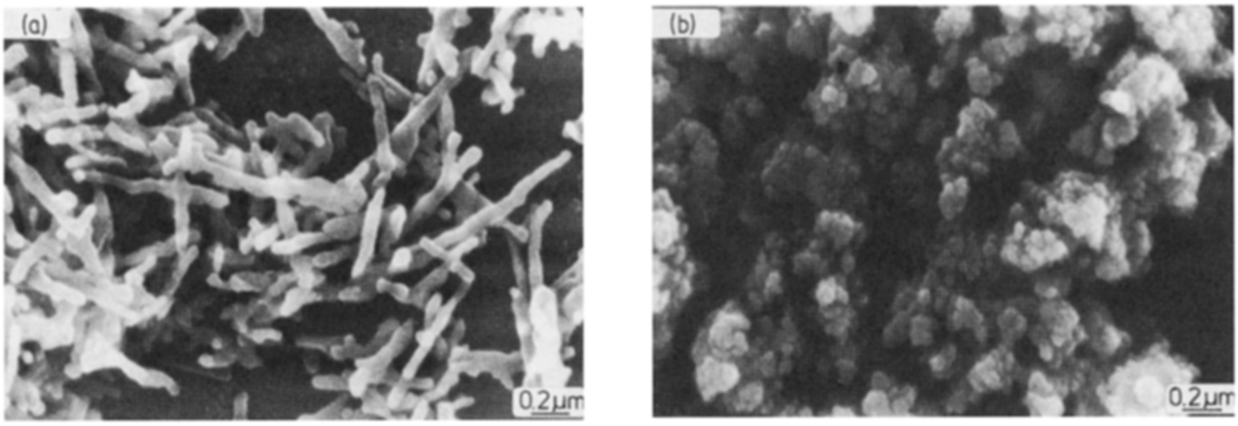

Figure 1 Micrographs of inorganic functional powders. (a) γ-Fe_2O_3; (b) RuO_2.

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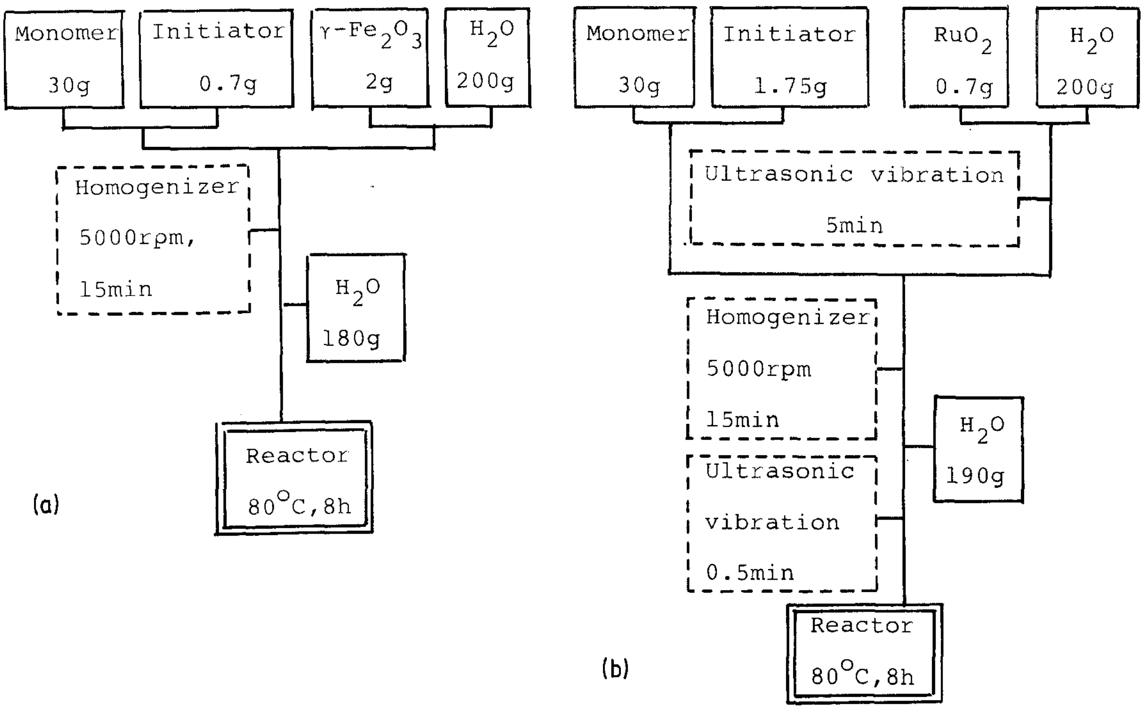

Figure 2 Schematic representation of the preparation of composites including: (a) γ-Fe_2O_3; (b) RuO_2.

2.2. Preparation of reaction mixture and polymerization

A standard procedure of preparing γ-Fe_2O_3–polystyrene composites is schematically shown in Fig. 2. 2 g γ-Fe_2O_3 was dispersed in 200 ml ion exchanged water. This suspension was mixed with 30 g monomer containing 0.7 g lauroyl peroxide as an initiator. The ternary complex disperse system was then mixed vigorously in a 300 cm^3 tall beaker with an homogenizer (Auto-Homomixer, Tokushu Kika, Tokyo) at 5000 rpm for 15 min. A final reaction mixture was obtained by subsequently adding 180 ml H_2O. The complex disperse system thus obtained consists of small monomer droplets surrounded by small inorganic particles at the monomer/aqueous phase boundary. The procedure was similar with RuO_2 as a fine powdery phase, except that the initiator and powder content were 1.75 and 0.7 g, respectively. A better dispersion of RuO_2 was attempted by irradiating ultrasonically the reaction mixture containing RuO_2. The composition of the mixture was changed systematically as shown in Table I.

Polymerization was carried out by putting the reaction mixture into a 500 cm^3 four-neck separable flask preheated at 80° C, stirred at 750 or 300 rpm for systems containing γ-Fe_2O_3 or RuO_2, respectively, for 8 h. The polymerized product was separated by filtrating and dried under a reduced pressure, 10 torr, at 25° C for 10 h.

2.3. Characterization of composite powders

The particle size distribution was obtained by a conventional sieve analysis. The fractional coverage of the inorganic powder by volume, i.e. the volume fraction of the inorganic powders with respect to the composite, θ, was obtained either by analysing the metallic content after leaching out by a diluted HCl solution or by the weight loss after burning out the polymer component by heating to 900 K in an oxygen atmosphere. The degree of polymerization was determined by a conventional intrinsic viscosity method by using diluted benzene solution.

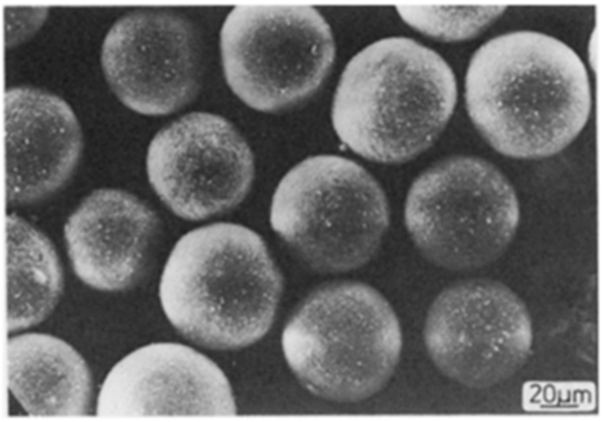

Figure 3 γ-Fe_2O_3/polystyrene composite microspheres.

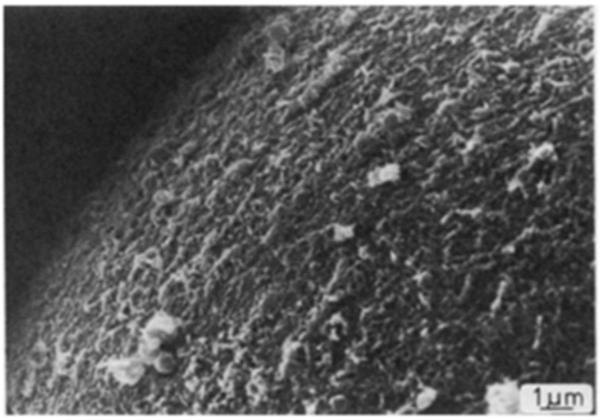

Figure 4 Surface of γ-Fe_2O_3/polystyrene composite.

TABLE I Composition of reaction mixture and properties of composites

Sample	Composition of reaction mixture					Yield	Av. diameter	Av. degree of polymerization
	H_2O (g)	Styrene (g)	γ-Fe_2O_3 (g)	RuO_2 (g)	Initiator (g)	(%)	(μm)	
S1	380	30	2.0		0.7	78	71	1720
F1	380	30	4.0		0.7	82	87	1350
F2	380	30	1.0		0.7	63	81	1180
W1	380	15	1.0		0.35	68	52	1600
W2	470	30	2.0		0.7	70	74	910
W3	290	30	2.0		0.7	81	96	1770
W4	380	45	2.0		0.7	68	50	830
I1	380	30	2.0		2.0	89	49	420
I2	380	30	2.0		1.4	80	50	640
I3	380	30	2.0		0.35	72	60	1760
I4	380	30	2.0		0.23	67	110	3600
S3	390	30		0.7	1.75	89	380	600
I5	390	30		0.7	2.46	89	360	340
I6	390	30		0.7	1.05	91	380	1450

3. Results and discussion

3.1. Yield of the composite

As long as the monomer globule was properly covered with the fine powdery material and we obtained composites in a dispersed form, the yield of the polymeric composite with respect to the total weight of the starting mixture was always higher than 70% and often reached 90%.

3.2. Microscopic observation of the composite surface

Typical scanning electron micrographs of the composite powders are shown in Figs. 3 to 7. Figs. 3 to 5 represent the γ-Fe_2O_3–polystyrene composite in its 200/270 mesh fraction. It was ascertained that the inorganic powder was located exclusively on the surface of the composite by using the electron probe microanalysis of the metallic ingredient. The surface of the spherical composite was covered with a densely packed layer of Fe_2O_3 as shown in Fig. 4. The fine particles at the surface do not seem to constitute a monolayer, but a multilayer. Powders at the outer layer must be bound together with those at inner layers by means of a cohesive force between powder particles.

On the surface of the composites, a number of very small spheres were often present, as shown in Fig. 5. These spheres are likely to be polystyrene microspheres as a result of partial emulsion polymerization [7].

The state of adhesion of RuO_2 on the surface of the polymer microsphere was also satisfactory, as shown in Figs. 6 and 7. Some surface aggregates were recognized, however, as shown in Fig. 7. The average size of the RuO_2 aggregates was approximately 2 to 3 μm.

3.3. Particle size of the composites

Some representative cumulative size distribution curves are shown in Fig. 8. While the mean diameter of γ-Fe_2O_3–polystyrene composites varied between 50 and 100 μm as summarized in Table I, the tails of the distribution ranged from 0.5 to 50 μm depending on the polymerization condition. By comparing Samples W1 and W3 with Sample S1, the latter being prepared under the standard condition (see Table I), the larger amount of the aqueous phase results in a smaller mean diameter and little narrower size distribution. When the amount of the monomer was larger, however, d_{50} did not increase (W4). Overdose of the initiator made the mean diameter smaller, although Sample I4 had a fairly d_{50}, presumably because of the coalescence at the early stage of polymerization. The amount of inorganic powder did not seem to play an important role with regard to the particle size of the composite. The average particle size of the composite including RuO_2 was approximately five times as large as those with γ-Fe_2O_3.

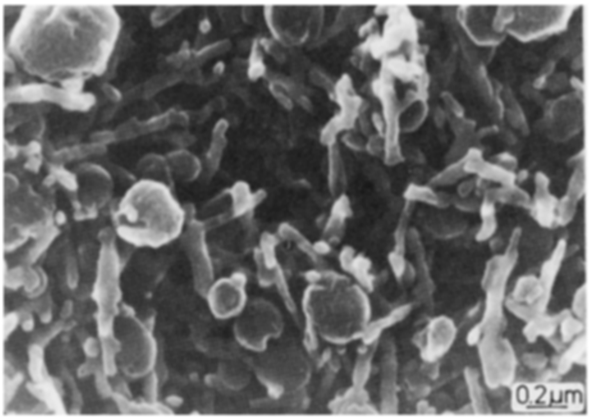

Figure 5 Surface of γ-Fe_2O_3/polystyrene composite at higher magnification.

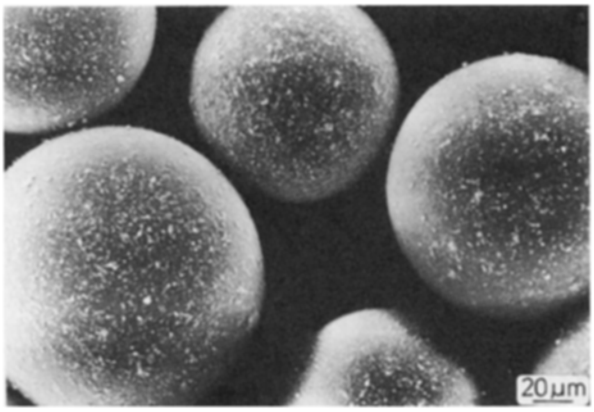

Figure 6 RuO_2/polystyrene composite microspheres.

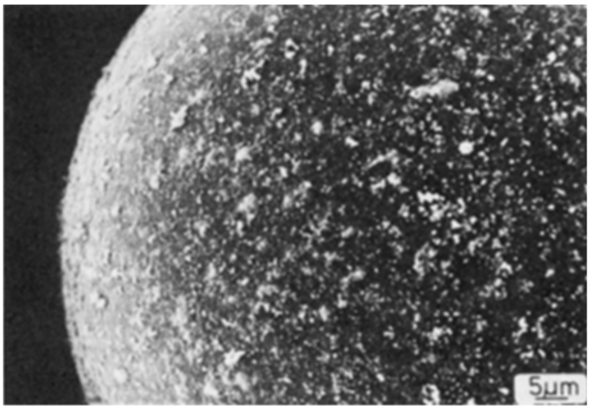

Figure 7 Surface of RuO_2/polystyrene composite.

3.4. Fractional coverage of the inorganic powder

The fractional coverage of the inorganic powder on the surface of the composite, θ, was larger with a smaller particle size. When θ was plotted against the reciprocal of the particle size, $1/d$, a straight line through the origin was obtained as shown in Fig. 9. This suggests that the fractional coverage is proportional to the specific surface area. This, in turn, implies that the amount of adhered powder per unit surface area is constant, irrespective of the particle size of the composite.

3.5. Degree of polymerization

When the amount of the initiator relative to the monomer was increased, the degree of polymerization decreased remarkably as shown in Fig. 10. The rate of polymerization, on the other hand, decreased with decreasing amount of initiator. As a result, a certain amount of unreacted monomer was detected even after 8 h polymerization in the case of Sample I4 which contained the largest amount of lauroyl peroxide. When the ratio of the initiator to the monomer was kept constant, the average degree of polymerization varied only between 900 and 1700 depending on the other reaction conditions. No significant variation of the degree of polymerization was observed for the composites with the varied particle size.

4. Conclusion

A simple consideration of the surface energy balance shows us that the solid particle favours being located at the monomer/water interface at equilibrium, as long as the contact angle of either liquid to the solid is larger than 0° and smaller than 180° [8], a condition which is fulfilled in most of the cases.

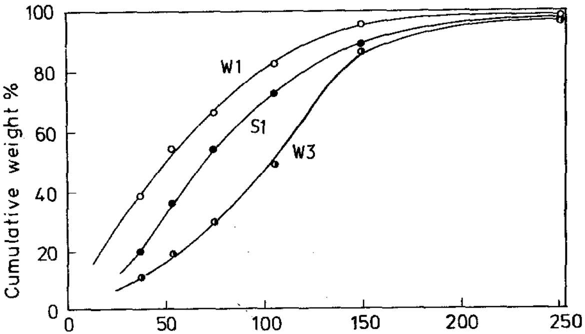

Figure 8 Particle size distribution of γ-Fe_2O_3/polystyrene composite microspheres.

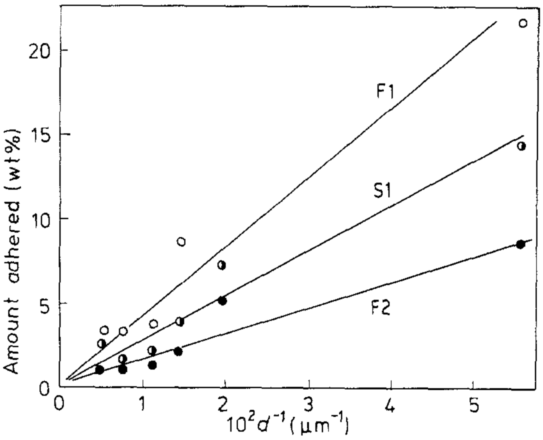

Figure 9 Relationship between fractional coverage, θ, or γ-Fe_2O_3, and $1/d$.

Nevertheless, preparation of the present composite was not always successful. Whether the inorganic powder is dispersed at first into an aqueous phase, or in a monomer phase, plays, for instance, a significant role. This immediately implies that the complex disperse system was not in general surface equilibrium.

Since the powder layer serves as a stabilizer of the monomer globule during polymerization, the difference in the average size and the size distribution of the composite spherical powder should be attributed to the surface energy state and the structure of the powder layer. The stabilizing ability of the powder layer at the monomer/water interface is now being studied.

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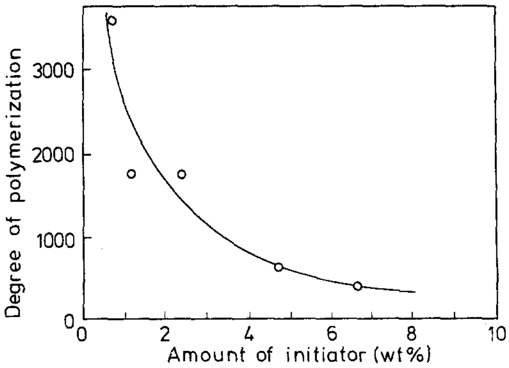

Figure 10 Relationship between degree of polymerization and amount of initiator for γ-Fe_2O_3/polystyrene composite.