

Magnetic compounds as coatings on polymer particles and magnetic properties of the composite particles

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Spherical micron-sized polymer particles coated with magnetite have been prepared by a new method consisting of a two step process, in which iron compounds are coated on a micron-sized polymer core by controlled hydrolysis of FeCl₃ in the presence of urea, poly(vinylpyrrolidone) and hydrochloric acid. The thickness of the coating layer could be altered by adjusting the amount of FeCl₃ added to the system. Magnetic particles were obtained by treating the coated powders with hydrogen at moderate temperatures. The chemical composition and morphology of the coating layer, and the resulting magnetic properties varied with the calcination conditions.

Introduction

In recent years, considerable effort has been devoted to the development of methods for the preparation of composite particles consisting of polymer cores covered with shells of different chemical composition.^{1–9} In several of these powders, particles covered with magnetic materials have been used or proposed as beads for cell separations, or as pigments, catalysts, coatings, flocculents, toners, etc.

Recently, it was shown that submicron-sized polymer particles can be covered with smooth inorganic layers by heterocoagulation with *in situ* formed basic yttrium carbonate³ and zirconium compounds,⁴ making it possible to extend the use of these colloids to different areas of technology. We propose to extend this technology to micron-sized polymer cores and to produce magnetic composite particles.

Magnetic powders have been prepared by controlled hydrolysis of FeCl₃ in the presence of polymer colloids, urea, PVP and hydrochloric acid, followed by calcination of the composite powders in a flow of hydrogen. The magnetic properties of the coated particles have been investigated.

Experimental

Materials

A cross-linked polymer latex [poly(divinylbenzene); 6.12 μm and 6.98 μm, DYNOL] was filtered off, washed with hot water and propan-2-ol, and then dried in a desiccator. Urea (Wako), poly(vinylpyrrolidone) (PVP; average molecular weight 360 000, Aldrich), iron(III) chloride hexahydrate (Wako), sulfuric acid (Wako), hydrochloric acid (Wako), and propan-2-ol (Wako) were used without further purification.

Preparation of particles

Sulfonated polymer latex. The purified polymer powders were treated with concentrated sulfuric acid for 2 h in an ice-cold bath. Then the systems were added to ice-cold water to discontinue the reaction and the resulting dispersions allowed to stand to allow them to settle. The separated particles were

resuspended in doubly distilled water, and then centrifuged at 6000 rpm for 20 min. This process was repeated four times, finally washing with propan-2-ol. The particles were then dried in a desiccator.

Coated particles. A reaction mixture containing various amounts of sulfonated polymer particles, 6.0 g of poly(vinylpyrrolidone) and 1 dm³ of distilled water was dispersed in an ultrasonic bath and heated at 95 °C and then 1.0 × 10^{−3} mol FeCl₃ and 0.1 mol urea were added. After ageing for 1.7 h, additional amounts of urea were added to the system, and then further iron(III) chloride solution was gradually added to the dispersion. The pH of the systems could be controlled by varying the rate of addition of the aqueous solution of FeCl₃. After ageing for 1 h after the addition of FeCl₃, the systems were quenched in cold water. In order to alter the thickness of the coating layer, the amount of FeCl₃ added to the system was varied systematically. The products were separated from the solution by filtration, washed with distilled water and then dried in a desiccator.

Calcined particles. In order to modify the chemical composition of the coating layer, the composite particles were heated at 270–330 °C in hydrogen at various flow rates for 0.5–3 h.

Analyses. The average particle sizes were determined by optical microscopy while the particle morphology was evaluated by scanning electron microscopy using a JEM-2000FX (JEOL) instrument. The coated particles were examined by X-ray powder diffraction using a MXP¹⁸ (Mac Science) instrument, while the magnetic properties of the particles were measured using a vibrating sample magnetometer (Riken).

Results and discussion

Preparation of coated particles

Heat resistant cross-linked polymer particles were used as the core materials taking into account the subsequent calcination treatments. The polymer powders used in this study could not be dispersed in water without a dispersing agent probably

Table 1 Effect of pH (controlled by rate of addition of an aqueous solution of FeCl₃) on the coating^a

Sample	pH ^b	System characteristics ^c
1	1.0	N
2	1.5	R
3	1.6	S
4	1.8	S
5	2.0	S

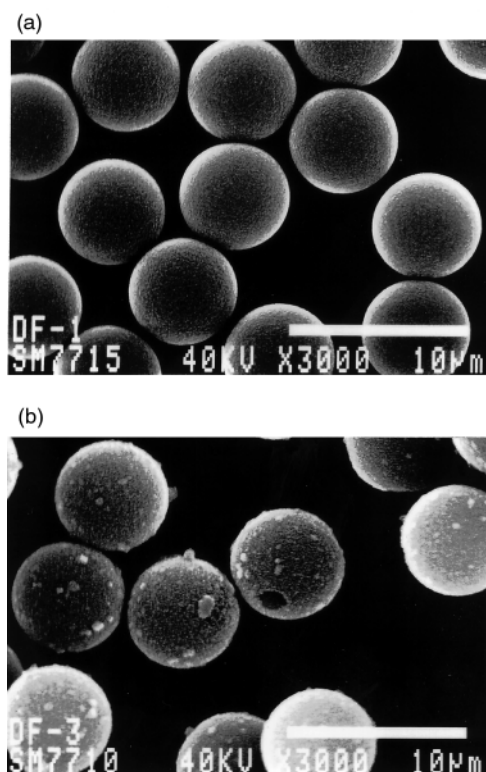
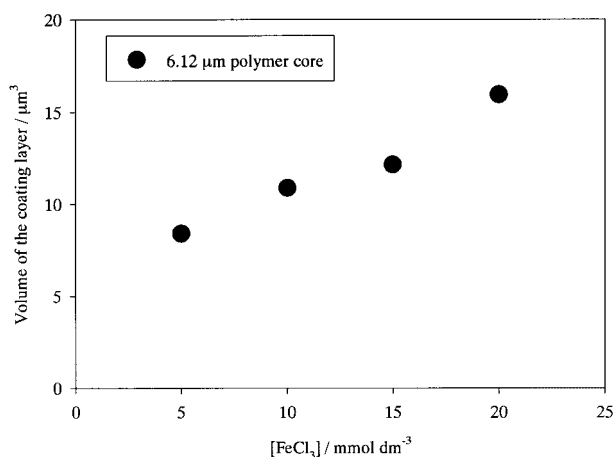
^aInitial concentrations: Sulfonated polymer latex (6.1 μm, 5 g dm⁻³), FeCl₃ (0.02 mol dm⁻³), PVP (0.6 wt%), urea (0.15 mol dm⁻³). Ageing for 1 h at 95 °C. ^b±0.1. ^cS; smooth-coated spheres, R; rough-coated spheres, N; non-coated particles.

because their surfaces were hydrophobic. The powders were therefore treated with concentrated sulfuric acid to generate hydrophilic sulfonated groups on the surface. Such treated particles could be dispersed in water and resulting good coverage of coatings was achieved, while no coating could be deposited on the non-treated latex.

The coating procedure consisted of controlled hydrolysis of aqueous solutions of FeCl₃ in the presence of the pretreated polymer latex. In order to prevent aggregation of core particles, polyvinylpyrrolidone (PVP) was added to the system.

We have previously reported that the mechanism for the coating of inorganic materials on the surface of polymer particles is based on heterocoagulation between the polymer core and inorganic particles formed *in situ* and subsequent growth of the inorganic shell.^{3,4} Previous reports also demonstrated that in the hydrolysis of FeCl₃, the morphology and composition of the precipitated iron compounds were influenced by the concentration of FeCl₃ and hydrochloric acid (H⁺) in the system.^{10,11} It appeared, therefore, that pH control in the system during hydrolysis of FeCl₃ was the key factor in obtaining good coatings.

The pH was maintained at a constant level by incremental addition of FeCl₃ aqueous solution, which cancelled any rise in pH owing to urea decomposition at elevated temperature.¹²

**Fig. 1** Scanning electron micrographs (SEM) of coated particles; (a) sample 5 and (b) sample 2.**Fig. 2** The relationship between the volume of the hematite shell and the molar concentration of FeCl₃ for systems prepared by gradually adding aqueous solutions of FeCl₃ and ageing at 95 °C. Initial concentrations: sulfonated polymer latex (6.12 μm, 5 g dm⁻³), hydrochloric acid (0.03 mol dm⁻³), PVP (0.6 wt%), urea (0.15 mol dm⁻³).

The effects of pH are summarized in Table 1. When the pH was <1.5 or >3, no-coated polymer particles were obtained. Fig. 1 shows powder particles encased with smooth coatings obtained when the pH in the system was controlled at *ca.* 2, whereas rough-coated polymer particles were obtained at pH 1.5. At pH ≤1.0, no coated polymer particles were obtained since hydrolysis of FeCl₃ did not occur. Good coverage of iron compounds was observed in the range pH=1.6–2.0. At pH 2 smooth-coated particles were obtained with a thick coating (Table 1, sample 5).

The influence on the coating of the amount of FeCl₃ added to the system was investigated and results are summarized in Table 2. Upon increasing the amount of FeCl₃ added to the system the coating layer became thicker. Fig. 2 shows the relationship between the volume of the coating and the amount of iron(III) chloride added to the system. The shell consisted of a mixture of hematite and FeOOH as ascertained by XRD (Fig. 3).

Preparation of magnetic particles

In order to alter the chemical composition of the coating layer to lead to magnetic properties, the coated polymer particles were calcined in an atmosphere of hydrogen. Table 3

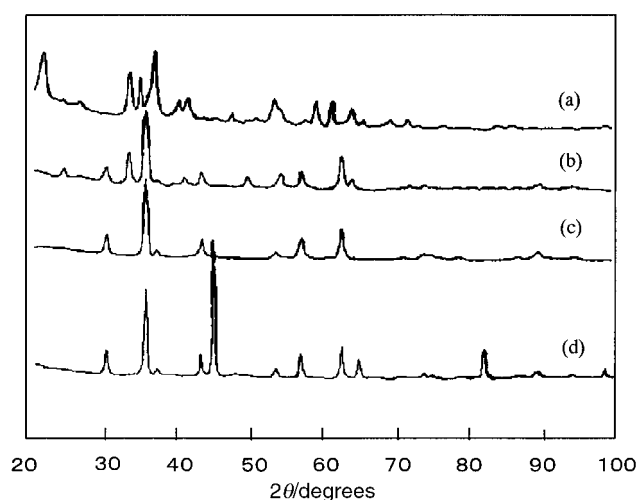
**Fig. 3** XRD patterns of composite particles: (a) hematite coated particles (sample 10) and magnetic particles; (b) sample 13, (c) sample 14 and (d) sample 17.

Table 2 Effect of the initial concentrations of FeCl₃ and polymer particles on the coating^a

Sample	[Polymer particles]/g dm ⁻³	[FeCl ₃]/mmol dm ⁻³	[Urea]/mol dm ⁻³	Coated particle diameter/μm	Shell content ^b (wt%)
6	5.0 ^c	5	0.15	6.26	2.0
7	5.0 ^c	10	0.15	6.30	3.8
8	5.0 ^c	15	0.15	6.32	10.7
9	5.0 ^c	20	0.15	6.38	15.3
10	20.0 ^d	74	0.60	7.18	13.0

^aInitial concentrations: PVP (0.6 wt%), hydrochloric acid (0.03 mol dm⁻³). Ageing for 1 h at 95 °C at pH=2.0±0.1. ^bEstimated from the yield of the product ([composite particles obtained]–[polymer particles])/[polymer particles]. ^c6.12 μm of polymer particles. ^d6.98 μm of polymer particles.

Table 3 Properties of magnetic particles obtained by calcination of the composite particles (sample 10) at different temperatures and times; flow rate of hydrogen = 0.2 dm³ min⁻¹

Sample	Calcination temperature/°C	Ageing time/h	Composition of the shell (wt%)		
			Hematite	Magnetite	Iron
11	290	1	64	36	0
12	290	2	3	97	0
13	310	0.5	56	44	0
14	310	2	0	100	0
15	330	1	0	100	0
16	330	2	0	80	20
17	330	3	0	54	46

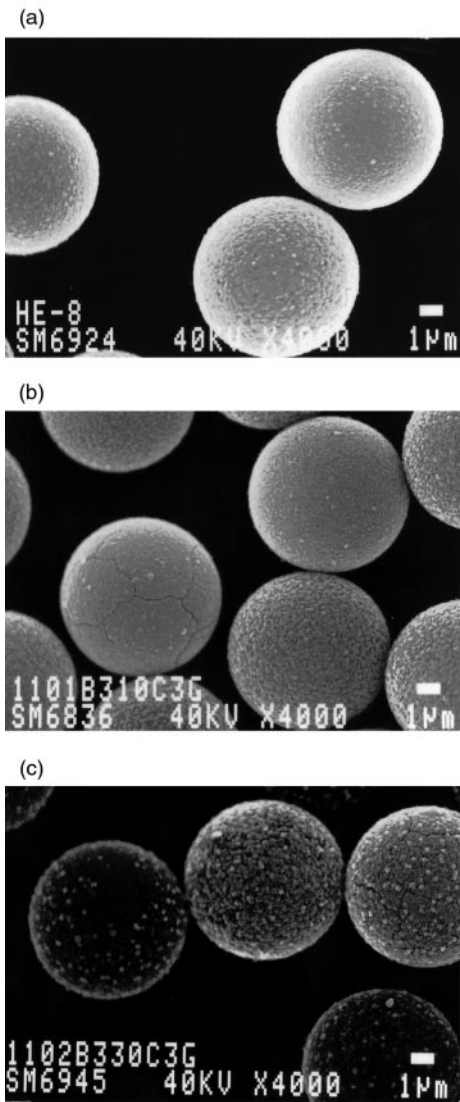


Fig. 4 SEM images of (a) composite particles (sample 10) and calcined particles (b) sample 15 (Table 3) and (c) sample 17 (Table 3).

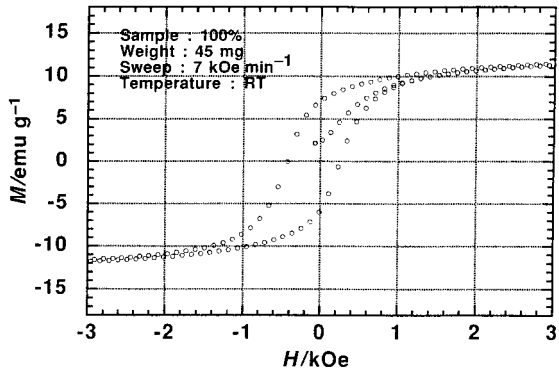


Fig. 5 *M*–*H* loops for calcined particles (sample 14).

summarizes the results obtained under different experimental conditions and XRD patterns of a variety of composite particles are shown in Fig. 3. The peaks in Fig. 3(a) are assigned to hematite and FeOOH, peaks in Fig. 3(b) are assigned to hematite and magnetite, peaks in Fig. 3(c) are assigned to magnetite whereas peaks in Fig. 3(d) are assigned to magnetite and iron. The amounts of magnetite in the calcined particles increased while the amount of hematite decreased as reduction proceeded. In addition, the more harsh the calcination conditions, the rougher the coated layer became. Fig. 4 illustrates powders encased in smooth and rough shells as well as original coated polymer particles. The composition of the shell varied with the calcination time and temperature. Severe reduction of the shell led to generation of metallic iron accompanied by a morphology change with the resulting shell layer becoming rough (Fig. 4). On the other hand, mild reduction of the coating layer led to a degree of non-reacted hematite, as ascertained by XRD (Fig. 3). The composition of the shell was pure magnetite under moderate calcination conditions (e.g. 330 °C for 1 h).

The magnetic properties of the calcined particles obtained under various reduction conditions are listed in Table 4. The saturation magnetization monotonously increased as the reduction of the shell layer proceeded while the residual magnetization increased until the hematite was completely

Table 4 Magnetic properties of the calcined composite particles

Sample	Composition of the shell (wt%)			Saturation magnetization/emu/g ⁻¹	Residual magnetization/emu g ⁻¹
	Hematite	Magnetite	Iron		
11	64	36	0	6.1	3.4
12	3	97	0	8.8	5.0
14	0	100	0	12.4	7.6
16	0	80	20	14.8	7.2
17	0	54	46	16.7	5.4

changed to magnetite. However, it then decreased as the ratio of iron in the shell increased. If magnetite particles are less than several nanometers in size, superparamagnetism is expected. According to SEM the size of the magnetite crystallites is 10–20 nm. Since, however, the *M–H* loops of calcined particles consisting of polymer cores covered with almost pure magnetite (sample 14) (Fig. 5) show ferromagnetic behavior, this suggests that the shell layer consists of several aggregated particles of larger size.

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