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SHORT COMMUNICATION

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Titanium compounds as coatings on polystyrene latices and as hollow spheres

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Abstract Sub-micron-sized anionic polystyrene latices have been coated with uniform layers of amorphous titanium dioxide by hydrolysis of titanium tetrabutoxide in ethanolic solutions containing the polymer cores. The thickness of the coating layer could be altered by adjusting the concentration of titanium tetrabutoxide and the amount of polymer latex added to the system. Hollow colloidal spheres of crystal titanium dioxide were obtained by calcination of the so-coated polystyrene latices at an elevated temperature.

Key words Titanium dioxide · Composite particles · Hydrolysis · Polymer latex · Calcination

Introduction

Previous reports have demonstrated the preparation of composite particles consisting of organic cores covered with inorganic shells [1–13]. Since the active surface sites can be altered by appropriate coatings, the properties of these composite dispersions (magnetic, optical, electric, adsorptive, etc.) may be adjusted to meet specific requirements for a given application. In addition, hollow particles have been of interest as fillers, coatings, capsule agents, etc., because of their lower density and optical properties [14–20].

Several studies have shown that inorganic cores as well as organic cores can be covered with inorganic shells by hydrolysis, in situ, of the corresponding metallic salt in the presence of core materials [21–26]. It has also been shown that the hydrolysis of metal alkoxides can be applied to deposit uniform layers of TiO_2 over ZnO or $Cu(OH)_2CuCO_3$ [27, 28]. In addition, several reports described hollow inorganic particles obtained by calcining polymer particles coated with uniform inorganic shells [4, 29].

This study demonstrates that the process previously described can be applied to other systems. Thus, the preparation of sub-micron-sized polystyrene particles coated with uniform layers of amorphous titanium compounds and hollow particles of titanium dioxide are described. The former was studied in detail using hydrolysis of titanium tetrabutoxide (TBOT) in the presence of a polystyrene latex. The latter, preparation of hollow titanium dioxide particles of a narrow size distribution, could then be obtained by calcining such coated particles at an elevated temperature in air.

Experimental

Materials

TBOT (Aldrich), poly(vinylpyrrolidone) (PVP, weight-average molecular weight = 360,000, Aldrich), styrene (Wako), ethanol (Wako), potassium persulfate (Wako), and sodium dodecyl sulfate (Wako) were used without further purification.

Preparation of particles

Polystyrene latex

An anionic polystyrene latex, used as core particles, was prepared by the batch polymerization method. For this purpose, the reaction was carried out in a 500-cm^3 container under the condition listed in Table 1. To eliminate the effects of oxygen, the solution was purged with nitrogen before the process was initiated. The polymerization was continued until the conversion exceeded 99%, as determined gravimetrically. The transmission electron micrograph (TEM) of the polystyrene particles prepared by this procedure (Table 1) is shown in Fig. 1.

Coated particles

The coating procedure consisted of controlled hydrolysis of ethanolic solution of TBOT in the presence of a polystyrene latex. In order to prevent aggregation of the core particles, PVP was added to the system. Thus, dispersions containing polystyrene latex, TBOT, and PVP were aged for different times in test tubes, tightly closed with Teflon-lined caps, placed in an oven preheated to 100 °C. After aging, the systems were quenched in a cold-water bath to discontinue the reaction. The resulting dispersions were centrifuged at 3500 rpm for 25 min, and the supernatant solutions were discarded, and then the particles were resuspended in doubly distilled water in an ultrasonic bath. This process was repeated four times, and the so-purified powders were dried in a desiccator.

Hollow particles

To produce hollow titanium dioxide particles, the polymer coated with the titanium compound was calcined for 3 h in air in a furnace at various temperatures at a rate of 10 °C min^{-1}.

Analyses

The average size of the dispersions was determined by transmission electron microscopy using a JEM-2000FX (JEOL). The coated and hollow particles were examined by X-ray diffraction (XRD) using an MXP[18] (Mac Science) and by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a TG/DTA300 (Seiko).

Table 1 The conditions used in the preparation of the polystyrene (*PS*) latex at 80 °C

Styrene (g)	65
Potassium persulfate (g)	0.65
Sodium dodecyl sulfate (g)	0.195
Water (g)	373
Particle size (μm)	0.42[a]

[a] Determined by electron microscopy

Results and discussion

Preparation of coated particles

The results obtained under different experimental conditions for the coating are summarized in Table 2. It was necessary to add a protective agent to the system in order to prevent aggregation of core particles without affecting the precipitation of titanium dioxide.

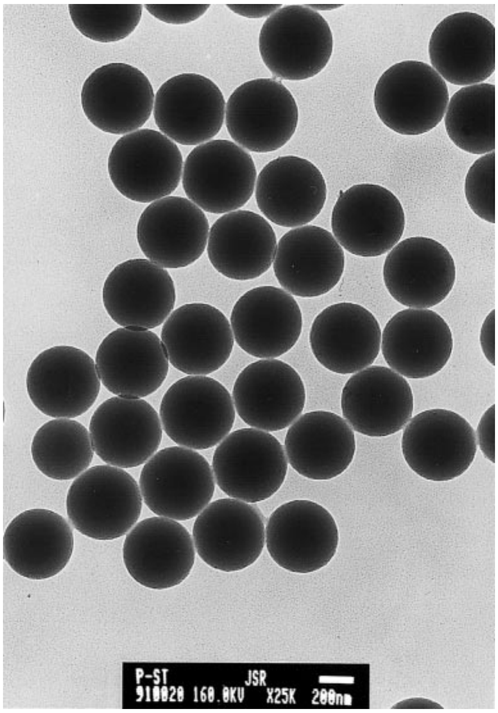


Fig. 1 Transmission electron micrograph (*TEM*) of polystyrene particles used as cores (Table 1)

Table 2 Properties of spherical coated particles obtained by aging at 100 °C for 1.5 h ethanolic dispersions containing 1.6 mol dm^{-3} H_2O in the presence of different amounts of PS latex, titanium tetrabutoxide (*TBOT*), and poly(vinylpyrrolidone) (*PVP*)

Sample	PS (g dm^{-3})	TBOT (mol dm^{-3})	PVP (g dm^{-3})	Coated particle diameter (μm)	Ratio of inner/outer diameter	System characterization[a]
1	1.5	1.8×10^{-2}	10	0.48	0.88	S
2	1.5	1.8×10^{-2}	–	0.48	0.88	A,S
3	1.5	0.5×10^{-2}	10	0.43	0.98	S
4	1.5	1.0×10^{-2}	10	0.44	0.95	S
5	1.5	2.0×10^{-2}	10	0.48	0.88	M
6	0.5	1.5×10^{-2}	10	0.48	0.88	M
7	1.0	1.5×10^{-2}	10	0.48	0.88	M
8	2.5	1.5×10^{-2}	10	0.45	0.93	S
9	5.0	1.5×10^{-2}	10	0.43	0.98	S

[a] S: smooth coated spheres; A: aggregated coated powders; M: mixed systems consisting of coated particles and separated titania particles

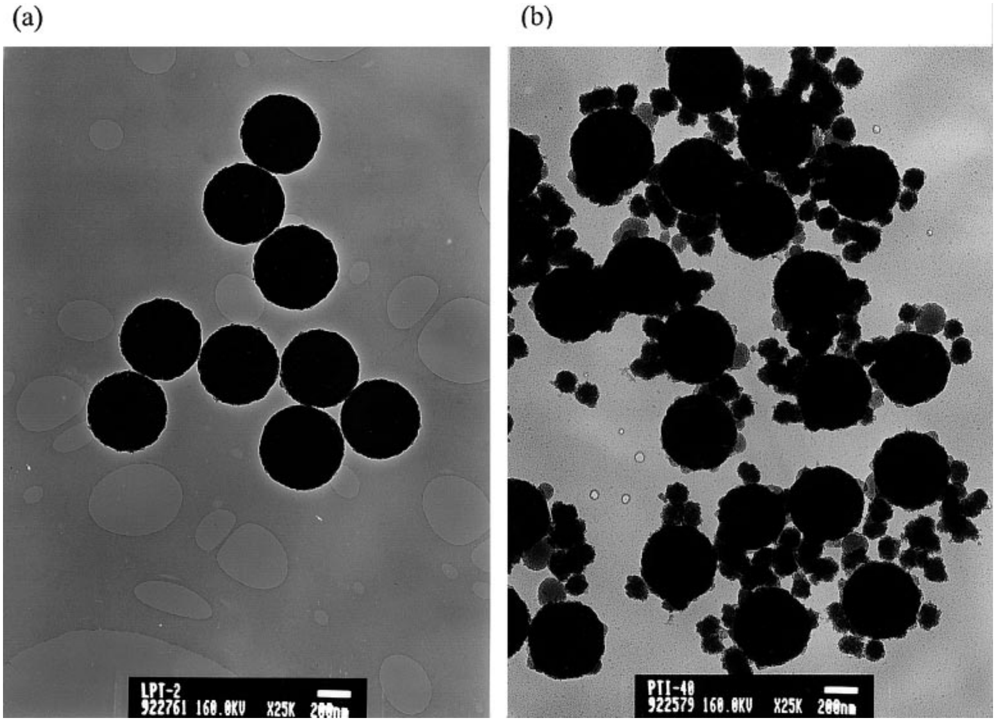


Fig. 2 TEM of particles obtained by aging at 100 °C for 1.5 h ethanolic solutions of 1.5 g dm^{-3} polystyrene particles and 1.6 mol dm^{-3} H_2O containing **a** 1.8 × 10^{-2} mol dm^{-3} titanium tetrabutoxide (*TBOT*) and 10 g dm^{-3} poly(vinylpyrrolidone) (PVP) (sample 1) and **b** 2.0 × 10^{-2} mol dm^{-3} TBOT and 10 g dm^{-3} PVP (sample 5)

PVP fulfilled these requirements, although other protective agents were not examined. To establish the optimum condition for the coating of the polystyrene latex, several parameters were varied systematically, including the concentrations of TBOT and the polystyrene latex.

It is quite evident that coating of titania on polymer particles was dependent on the concentrations of the particles and TBOT in a given system; when the latter was in excess, separated titania particles were generated as well as the coated latex (designated by “M” in Table 2). The TEMs in Fig. 2 illustrate powders enhanced in a smooth shell (S) as well as an example of mixed dispersions (M) consisting of coated particles and free titania particles.

The thickness of the coating layer could be altered by adjusting the concentration of TBOT and the amount of polymer latex added to the system. The relationship between the volume of the coating and the amount of TBOT is shown in Fig 3. The particle diameter increased from 0.42 μm (core size) to 0.48 μm on coating. Over the lower range of TBOT concentrations (about 0.018 mol dm^{-3}), no extraneous particles of titania were prepared; however, the addition of more than 0.020 mol dm^{-3} TBOT to the system resulted in the appearance of mixed dispersions. The relationship between the volume of the coating layer and the amount of polymer core added to the system in the presence of same amount of TBOT (0.015 mol dm^{-3}) is shown in Fig. 4. In this case, the particle diameter also increased to 0.48 μm on coating; however, free titania particles were generated when less than 1.0 g dm^{-3} polystyrene latex was added to the system.

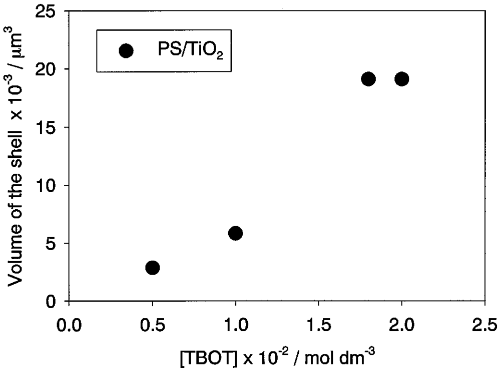


Fig. 3 The relationship between the volume of the TiO_2 shell and the molar concentration of TBOT for the systems prepared by aging at 100 °C for 1.5 h ethanolic dispersions of 1.5 g dm^{-3} polystyrene particles, 1.6 mol dm^{-3} H_2O, and 10 g dm^{-3} PVP in the presence of different amounts of polystyrene

It is of interest to establish the actual mechanism for the formation of the coating layer, although it has not been ascertained. An analogous explanation is applied to the mechanism of the heterocoagulation between polymer cores and the titanium compound particles formed in situ, and the successive growth of the coating layer may be followed as the hydrolysis of TBOT proceeds.

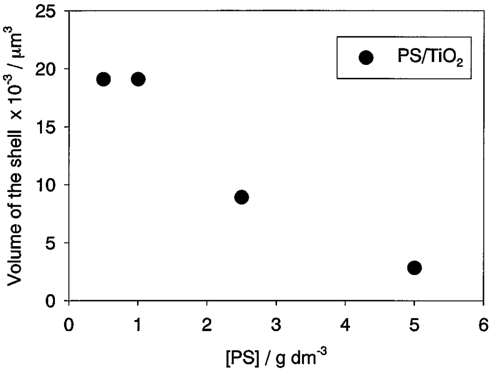


Fig. 4 The relationship between the volume of the TiO_2 shell and the concentration of the polystyrene particles for the systems prepared by aging at 100 °C for 1.5 h ethanolic dispersions of 1.5×10^{-2} mol dm^{-3} TBOT, 1.6 mol dm^{-3} H_2O, and 10 g dm^{-3} PVP in the presence of the different amounts of polystyrene

Table 3 Effects of the calcination temperature on the particle component and the morphology (heating rate of 10 °C min^{-1})

Sample	Original sample (Table 1)	Calcination temperature (°C)	Component of TiO_2
10	1	250	Amorphous
11	1	600	Crystalline (anatase)
12	1	750	Crystalline (anatase + rutile)
13	1	900	Crystalline (rutile)

Preparation of hollow particles

Voids are produced by complete thermal decomposition in air of polystyrene cores within coated particles. In order to establish the optimum condition for the preparation of hollow titania particles, the calcination temperatures were varied systematically, as summarized in Table 3.

The TEMs in Fig. 5 illustrate particles obtained under the conditions described. The TEM of coated

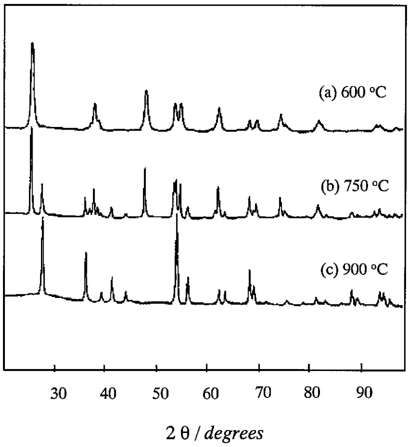
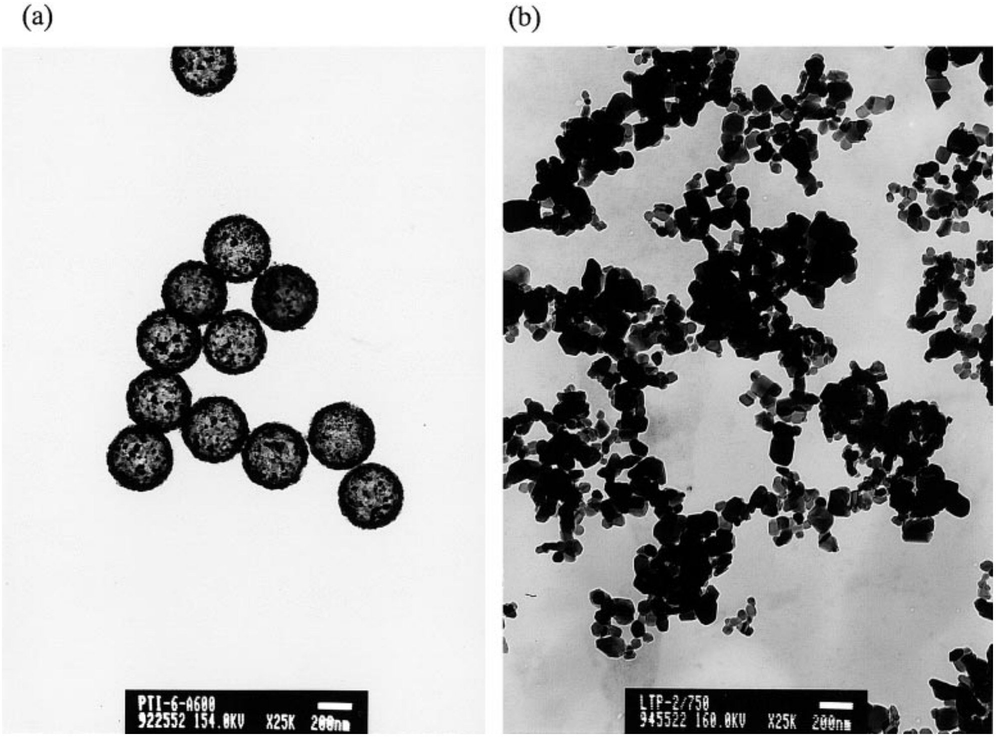


Fig. 6 X-ray diffraction patterns of **a** composite particles (sample 1) and of the same samples calcined at **b** 600 °C, **c** 750 °C, and **d** 900 °C (sample 13)

Fig. 5 TEM of particles obtained by calcining the composite particles (sample 1) in air for 3 h at **a** 600 °C (sample 11) and **b** 900 °C (sample 13)



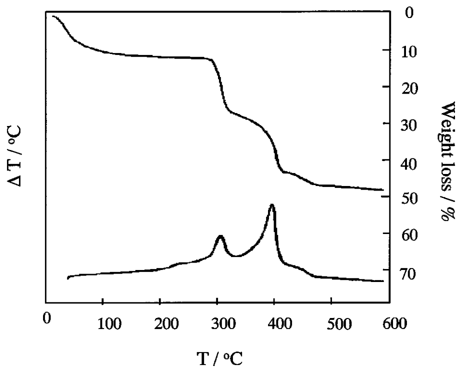


Fig. 7 Thermogravimetric analysis and differential thermal analysis curves of the composite particles (sample 1)

particles heated at 600 °C shows only hollow titania particles, while the TEM of the same powder calcined at more than 750 °C shows only recrystallized particles.

The XRD patterns in Fig. 6 demonstrate the components of TiO_2 powders given under the conditions described. When the coated particles were calcined at 250 °C for 3 h, the colloids remained amorphous; when they were calcined at 600 °C, the colloids became crystalline (anatase). When the coated particles were calcined at 750 °C, two peak patterns, which were characteristic of anatase and rutile types of TiO_2, were obtained, and when they were calcined at 900 °C, only recrystallized TiO_2 particles in the form of rutile TiO_2 were obtained.

The TGA curve of coated particles is illustrated in Fig. 7. The first weight loss estimates the release of water between 50 and 250 °C, whereas the second weight loss estimates the decomposition of core particles between 280 and 430 °C. Figure 7 also shows the DTA curves of coated particles. The exothermic peaks at 400 °C correspond to crystallization of amorphous TiO_2 into anatase, as confirmed by XRD. The transformation of anatase into rutile could not be clearly detected by DTA; however, the XRD indicated that such a process took place between 700 and 900 °C, the results almost coinciding with a previous report [6].

Thus, it is noteworthy that hollow titania particles in the form of the crystalline anatase component can be produced. An alternative approach is needed to synthesize the hollow titania particles in the form of the crystalline rutile component which are industrially more interested.

Conclusion

Composite particles containing a polymer core and an amorphous titania shell could be prepared by hydrolysis of TBOT in the presence of the polymer latex. The thickness of the coating layer be controlled by the concentration of TBOT and the amount of polymer latex added to the system. Hollow titania particles of a narrow particle size distribution could be obtained by calcining the composite particles at elevated temperature in air.

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