Preparation of Organic–Inorganic Nanocomposites with Core-Shell Structure by Inorganic Powders

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ABSTRACT: Organic–inorganic nanocomposites with core-shell structure were prepared in two steps. In the first step, the latex particles in the semibatch emulsion polymerization of butyl methacrylate (BMA), in the presence of methacrylic acid (MAA), were prepared. Small amounts of acrylic acid incorporated into the latex to have better interaction between the surface of particles and inorganic phase. MAA also increased the latex stability and decreased the amount of coagulum. In the second step, the core-shell structures were prepared by coating the latex particles with three types of inorganic powders. Pectin coated precipitated calcium carbonate, alumina, and silica. The examinations show that pectin-coated calcium carbonate has the best response than other types of calcium carbonate. Alumina was the second type of inorganic powder that was used for coating the core particles. Silicagel and fumed silica (Aerosil) were used for coating by silica. Scanning electron microscopy and transmission electron microscopy showed the particle morphology and the core-shell structure, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2943–2950, 2006

Key words: core-shell; nanocomposite; organic–inorganic materials; encapsulation; butyl methacrylate (BMA); methacrylic acid (MAA); powder; silicagel; Aerosil

INTRODUCTION

Core-shell materials consist of a core structural domain covered by a shell domain. The core and shell domains may be composed of a variety of materials including polymers, inorganic solids, and metals. Core-shell materials are typically spherical in shape; however, other shapes are possible. Advances in the preparation of core-shell materials have been reviewed recently.[1]

The fabrication of colloidal materials with desired structural, optical, and surface properties have recently been the subject of intense investigations.[2–8] Facile and flexible strategies that afford fine control over the synthesis and modification of particles are of paramount importance in building new classes of colloids.[9] Composite particles, often comprised of a solid core surrounded by a well-defined shell layer, are known to exhibit unique and enhanced characteristics over single-component colloids, making them attractive for use in a wide range of applications.[5,8,9] A commonly employed route to creating composite colloids is the postsynthesis modification of core particles, for example, by coating and/or encapsulating them with thin polymer or inorganic shells. Procedures to achieve this have predominantly relied on the *in situ* synthesis of polymer layers[2,7] or surface reactions (e.g. precipitation and sol–gel condensation) to deposit a range of inorganic layers onto preformed cores.[3–6,8] Recently, an alternative and remarkably adaptable approach, termed the layer-by-layer (LbL) self-assembly technique,[10,11] has been applied to the coating of colloids.[9,12] The basis of this method is the electrostatic association between alternately deposited, oppositely charged species.[11] Multilayered shells of polyelectrolytes,[13–15] inorganic nanoparticles,[16–20] or proteins[21–24] have been deposited onto particle templates, giving rise to novel colloidal entities. Organic–inorganic composite particles, comprising latex cores and silica nanoparticles,[16,17] luminescent semiconductors (CdTe),[18,19] or iron oxide nanoparticle multilayer coatings[20] have been fabricated. An interesting extension of these tailor-made core-shell particles has been the subsequent removal of the template cores, resulting in hollow capsules.[12,25–30] Although a variety of hollow capsules of polymers have been produced already,[25–28] to date only silica,[29] zeolite,[30] and magnetic[31] hollow spheres have been fabricated using this strategy.

The synthesis of uniform-sized hollow microspheres (size range of tens of nanometers to several millimeters),[31] in liquid or solid form, has gained increasing attention in recent years. Hollow spheres represent a special class of materials, which are of interest in the fields of medicine, pharmaceutics, materials science, and the paint industry; they find diverse applications, including encapsulation of products (for the controlled release of drugs, cosmetics, inks, and

TABLE I
Sample Washing Conditions

Volume ratios (ethanol/water)	Time (min)
50/50	15
25/75	15
10/90	15
0/100	15

dyes), the protection of light-sensitive components, catalysis, coatings, composites, and fillers.[31]

There exist a number of fabrication methods that are capable of producing a broad range of hollow microspheres. These include nozzle-reactor systems (spray drying or pyrolysis), and emulsion/phase separation techniques coupled with sol–gel processing.[1] Various hollow polymer, metal, and glass composite microspheres have been produced using nozzle-reactor methods.[31–36] The size of the microspheres, generally in the micrometer size range, is limited by the nozzle technology. Emulsion/phase separation procedures, however, offer the opportunity to create microspheres in the nanometer size range: single and mixed ceramic oxides have been processed.[31,37] Ceramic hollow microspheres, with micrometer diameters, have also been fabricated.[31] Yet, another method to produce hollow microspheres is to employ sacrificial cores: in this approach, a coating is deposited on the core as a result of controlled surface precipitation of inorganic molecular precursors from solution or direct surface reactions,[38] and the core can be subsequently removed by heating (calcination) or by dissolution in a solvent.[38,39]

More recently, hollow silica spheres were generated by emulsion polymerization coupled with sol–gel processing of tetraethoxysilane on the surface of poly(butyl methacrylate-co-methacrylic acid) particles, followed by calcination. By using a similar method, monodisperse, hollow silica nanoparticles have been produced by chemically dissolving the cores.[40]

EXPERIMENTAL

Materials

The chemicals used, butyl methacrylate (BMA) and methacrylic acid (MAA), were obtained from Merck chemical Co. They were purified by distillation under

TABLE II
Ethanol Elimination Conditions

Volume ratios (ethanol/epoxy resin)	Mixing time (h)
1/1	1
½	2
1/3	6
0/1	6

TABLE III
Optimized Conditions of Semibatch Emulsion Polymerization

	Reaction 1	Reaction 2
IRC		
H_2O(mL)	60.5	60.5
SLS(g)	0.36	0.36
BMA(mL)	3	3
MAA(mL)	—	0.10
IS	4	4
H_2O(mL)	0.16	0.16
$K_2S_2O_8$(g)		
MEF	20	20
H_2O(mL)	0.34	0.34
SLS(g)	52	52
BMA(mL)	—	1.35
MAA(mL)		

IRC, initial reactor charge; IS, initiator solution; MEF, monomer emulsion feed.

reduced pressure and were stored in a dark bottle at −5°C until requirement. Potassium persulfate ($K_2S_2O_8$) as initiator and sodium lauryl sulfate as emulsifier were supplied by Merck. $K_2S_2O_8$ was kept at −5°C and was used as received. Pectin-coated precipitated calcium carbonate (with average diameter of 5 μm) was supplied in technical grade from micronized powder (Iran). Alumina and silicagel were obtained from Merck. Fumed silicon dioxide (Aerosil™, with average diameter of 12 nm) was obtained from Sigma. The water used in all experiments was deionized and distilled in two stages.

Equipments

The samples were characterized by scanning electron microscopy (SEM; ZEISS DSM 960A) and transmission
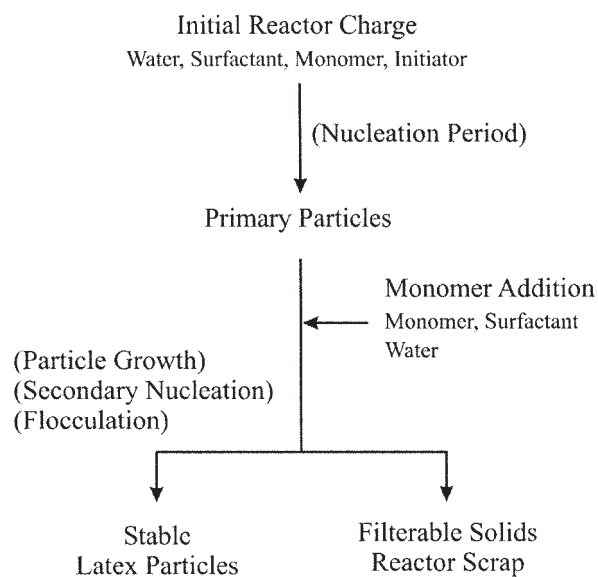
Initial Reactor Charge
Water, Surfactant, Monomer, Initiator

(Nucleation Period)

Primary Particles

Monomer Addition
Monomer, Surfactant
Water

(Particle Growth)
(Secondary Nucleation)
(Flocculation)

Stable
Latex Particles

Filterable Solids
Reactor Scrap

Figure 1 Scheme of semibatch emulsion polymerization.

Stable Latex Particles

| Powder addition
(Dispersed Powders in Water)

Particles With Core-Shell Structure

Centrifuge for 10 min
With 3000 rpm

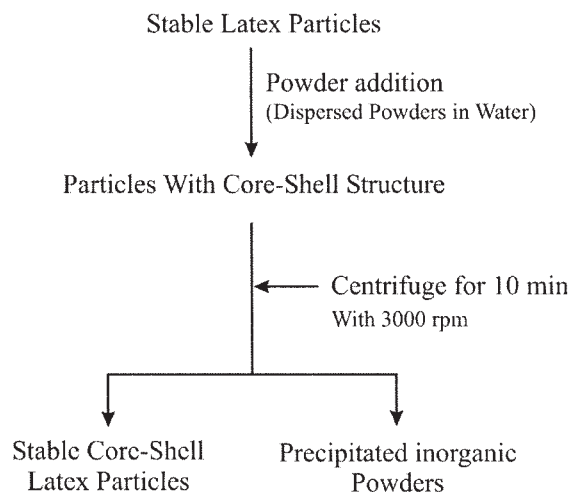Stable Core-Shell Latex Particles — Precipitated inorganic Powders

Figure 2 Scheme of encapsulation process.

electron microscopy (TEM; ZEISS 10C TEM). They were microtomed by using an ultramicrotom (LEICA ULTRACUT UCT).

Characterization

For SEM analysis, the emulsion samples were diluted in water 1 : 1000 (v/v). A drop of diluted emulsion was placed on the sample holder and was dried under freeze-drying. They were then placed under vacuum, flushed by argon, evacuated, and coated by powered gold.

Each of these emulsion samples was diluted in water 1 : 100 (v/v) for TEM analysis. This diluted emulsion was stained with 2% aqueous solution of OsO_4. After 1 h, the sample was washed with distilled water and the water was removed according to the schedule given in Table I. The procedure given in Table II was followed to eliminate the ethanol before treating the samples with epoxy. The samples were centrifuged for 6 h in epoxy resin and were molded at 60°C for 24 h. The molded samples were ultramicrotomed with a 70-nm thick glass knife and were picked up from the
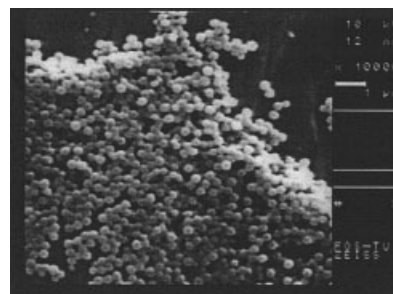

Figure 4 Photomicrograph of core particles (BMA-*co*-MAA) from reaction 2.

surface of distilled water onto annealed copper grids with a mesh size of ~1 mm.

Polymerization process

Polymerization was carried out in a 250-mL glass reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a reflux condenser. The polymerization procedure is described as follows. All process water, along with the initial surfactant, and monomers were charged to the reactor at room temperature. The initial reactor charge was purged with nitrogen for 10 min to remove the dissolved oxygen while the reactor temperature was brought to 80°C. The reaction was then initiated by adding the initiator solution to the reactor. After 15 min, the monomer emulsion was fed to the reactor over 180 min drop by drop with dropping. The polymerization temperature was kept at 80°C throughout the reaction. After the end of the monomer emulsion feed, the reaction system was maintained at 80°C for 1 h to reduce the level of the residual monomer. Table III shows the optimized amount of materials. The reaction scheme is shown in Figure 1.

In the designed experiments, all of the reaction variables were maintained constant except of the levels of MAA. A typical recipe for the semibatch emulsion polymerization of BMA with two levels of MAA is shown in Table III. MAA was not used in the reaction

Figure 3 Photomicrograph of core particles (BMA) from reaction 1.
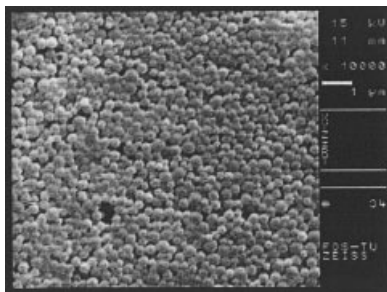

Figure 5 Photomicrograph of pectin-coated calcium carbonate.

Figure 6 Photomicrograph of core-shell particles with a layer of calcium carbonate (core is BMA).

Figure 8 Photomicrograph of core particle operated at 10 kV.

1 and the generated latex particles were poly(butyl methacrylate) (PBMA), while in the reaction 2, 3% of MAA incorporated into the reaction for preparing poly(butyl methacrylate-*co*-methacrylic acid). Figures 3 and 4 are photomicrographs of the core particles prepared from reactions 1 and 2, respectively.

Encapsulation of core particles

The core-shell structure was prepared by coating the latex particles. Three types of inorganic powder used for coating the core particles were pectin-coated precipitated calcium carbonate, alumina, and silica. Figure 5 is the photomicrograph of pectin coated precipitated calcium carbonate. Silicagel and aerosol have been used for coating the particles by silica.

In all of the experiments, 5 wt % of powder dispersed in water, then it was added to the latex drop by drop in 3 h at 70°C. Subsequently, the mixture was stirred for a future 1 h to complete the reaction. The resulting dispersion was centrifuged for 10 min with 3000 rpm three times to precipitate and remove the excess powder that was not coated the core particles. Figure 2 shows the encapsulation process.

Heating the samples

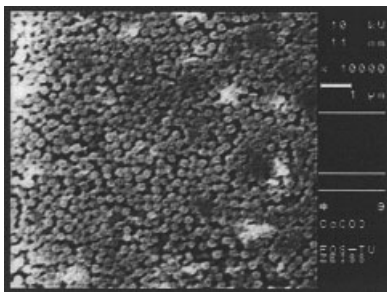In all of the samples, we use programmable oven to reach the target temperature (100, 400, and 500°C). The

increasing rate of temperature is 2.5°C/min and after reaching the target temperature, it was held constant for 3 h.

Hollow nanosphere fabrication

The first step in the fabrication of the hollow spheres was to prepare colloidal core-nanocomposite multi-layer shell particles. Hollow silica spheres were produced by drying the polymer lattices coated with SiO_2 multilayers on quartz slides at room temperature, and then calcining (heating rate 5°C/min) to 500°C and further 3 h to ensure complete core removal.

RESULTS AND DISCUSSION

The latex particles in the semibatch emulsion polymerization of BMA, in the presence of MAA, were prepared. Small amounts of acrylic acid incorporated into the latex to have better interaction between the surface of particles and inorganic phase. MAA also increased the latex stability and decreased the amount of coagulum.[41]
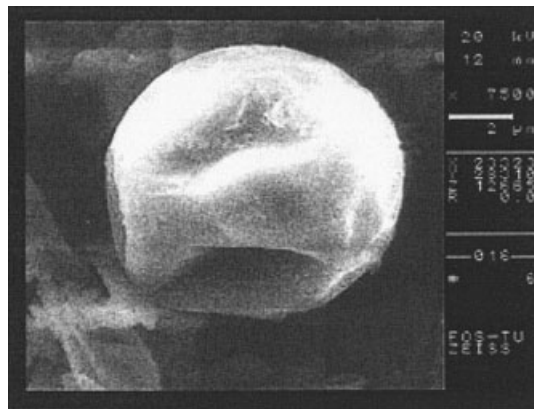

Figure 7 Photomicrograph of core-shell particles with a layer of calcium carbonate (core is BMA-*co*-MAA).

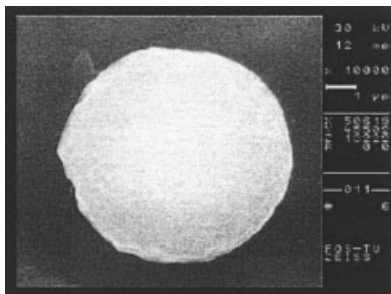
Figure 9 Photomicrograph of deformed core particle operated at 20 kV.

Figure 10 Photomicrograph of core-shell particles after operating at 30 kV (with complete rigid layer of calcium carbonate).

Figure 12 Photomicrograph of core-shell particles with a layer of alumina.

Encapsulation by calcium carbonate

Organic core particles do not coat by $CaCO_3$ easily, because either $CaCO_3$ coagulates in water or does not have a good interaction with core. To prevent the phase separation is important to reach a better interaction between organic and inorganic phases. Surface-treated grades of calcium carbonate are commercially available. Pectin is one of the surface treatments of choice. Pectin has a good interaction with water. It allows to improve the dispersion of $CaCO_3$ in water and, therefore, reduce the agglomeration. In addition, pectin has an interaction with organic phase, and so it causes to place $CaCO_3$ on the particles easily.[42] Photomicrographs in Figures 6 and 7 are coated-core particles (from reactions 1 and 2, respectively) with a thin layer of $CaCO_3$. Rough layer on the particles in SEM micrograph indicates that $CaCO_3$ particles are at the surface of nanocomposite particles and these particles have core-shell structure.

In the reaction 1, cores are PBMA that have T_g about room temperature.[43] It is easily deformed by increasing the temperature. This deformation is more sensible for the bigger particles in each latex sample. During scanning the particles in high voltage (20 kV) to take SEM micrograph, the temperature of the particles in scan areas increases a few degrees and the particles are deformed. We can use it to prove the core-shell
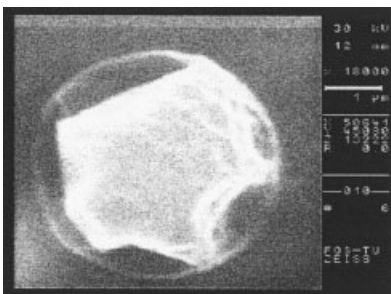
structure of the particles. Figure 8 shows one of these core particles in low voltage (10 kV). Increasing the operating voltage to 20 kV causes deformation of the core particles. Figure 9 shows one of these deformed core particles.

In core-shell systems with inorganic layer such as $CaCO_3$, there is a rigid shell on the core and so the core of the particles is deformed, while shell is not deformed by increasing the temperature. Figure 10 shows one of the core-shell particles with complete rigid shell, and so within the sphere is not seen in SEM micrograph. If the coated layer on the core is not complete, we can see within the sphere in SEM micrograph (Fig. 11). Deformed core and spherical shell have been shown in the image. This image shows the core-shell structure of the system.

Encapsulation by alumina

Alumina, because of its organophilic properties,[44] is suitable to coat the organic colloidal particles. Two different areas of the sample have been shown in Figures 12 and 13. One of them has many particles (Fig. 13), whereas the other one does not have (Fig. 12). The SEM micrographs show a rough layer on the particles. Also, they indicate that the surface of nanocomposites has been coated by alumina particles and these particles have core-shell structure.

Figure 11–Photomicrograph of core-shell particles after operating at 30 kV (while the layer of calcium carbonate is not complete).

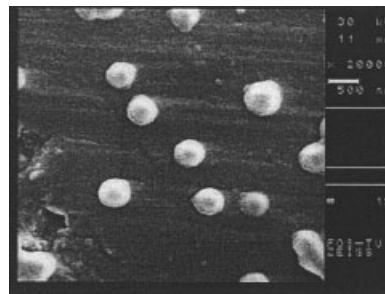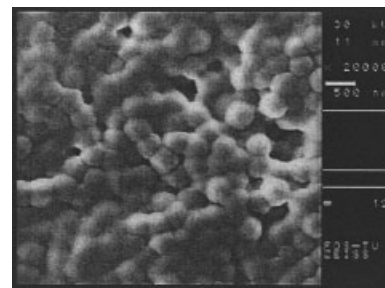**Figure 13** Photomicrograph of core-shell particles with a layer of alumina.

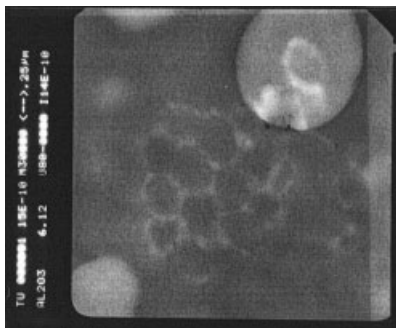**Figure 14** TEM micrograph of core-shell particles with a layer alumina.

Figure 16 TEM photomicrograph of core-shell particles with a layer of silicagel.

TEM studies of 70 nm cross sections direct evidence that these copolymer/alumina nanocomposites have alumina on their surface. Figure 14 shows a typical TEM image for polymer core/alumina shell; the observed black and white regions are attributed to the copolymer and alumina component, respectively.

Encapsulation by silica

Silica can be made to increase hardness, elastic recovery, scratch resistance, and resistance to heat distortion. Synthetic silicas are very fine amorphous white powders. Fumed, precipitated, and gel silica. Silicagels are chemically modified with organic waxes or inorganic fluorides with high surface areas (200–300 m^2/g). Typical loading levels of wax may be as high as 10% based on the weight of silica.[45] Fumed silica (Aerosil) is prepared by a high-temperature vapor process in which silicon tetrachloride is hydrolyzed in a flame of hydrogen.[46]

Silicagel, because of its wax, has a good interaction with organic materials. Rough layer on the particles, such as $CaCO_3$, in SEM micrograph indicates that the powder is on the surface of nanocomposites and the core-shell structure has been prepared (Fig. 15). Figure 16 shows a typical TEM micrograph for polymer core/silicagel shell; the observed black and white regions
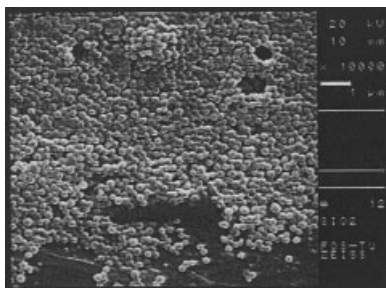
are attributed to the copolymer and alumina component, respectively.

Also, during scanning to take the SEM micrograph of reaction 1 particles, increasing the voltage to 30 kV causes deformation of the core of these particles. When the temperature increases above T_g point of the polymeric cores, these cores deformed easily and separated from its rigid inorganic layer (Fig. 17).

Fumed silica (Aerosil), with a diameter of ~12 nm, disperse in water and coat on the core particles easily. Figures 18 and 19 shows these core-shell systems with a thin layer of fumed silica. The bigger particles in the SEM image are related to the big Aerosil particles that can not coat the cores and can not be separated with centrifugation in 3000 rpm.

Figure 17 Photomicrograph of core-shell particles after operating at 30 kV (while the layer of silicagel is not complete).

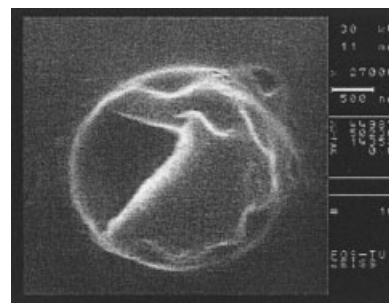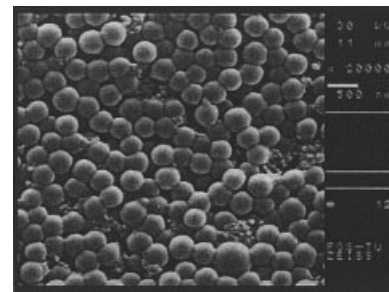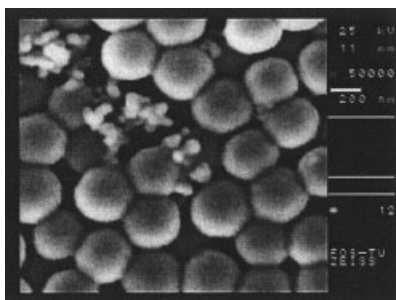**Figure 15** SEM photomicrograph of core-shell particles with a layer of silicagel.

Figure 18 Photomicrograph of core-shell particles with a layer of Aerosil.

Figure 19 Photomicrograph of deformed core-shell particles with a layer of Aerosil (zoom in Fig. 17).

Figure 22 Photomicrograph of core-shell particles with a layer of silicagel after remaining in 100°C for 3 h.

Thermal behavior of core-shell systems

Considering T_g of samples are lower than 100°C, we conclude that with putting these samples in this temperature, the particles deform easily and glue together. Figure 20 is related to homopolymer sample, which has been placed in 100°C for 3 h. Then it will be seen that most of the particles are glued together. Comparing this SEM micrograph with Figure 3, which is related to core particles, it can be concluded that heating the particles up to 100°C causes gluing the core particles together, whereas in core-shell samples with a layer of $CaCO_3$ (Fig. 21), particles are separated and not gluing together. Figure 22 shows core-shell particles with a layer of silicagel after heating to 100°C.
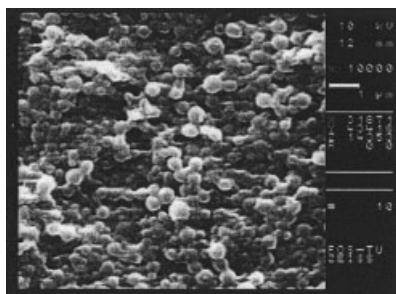
Hollow silica microspheres

Using the electrostatic sequential adsorption technique, the thickness of the nanocomposite multilayer shell surrounding the colloidal particles can be tailored depending on the number of silicagel layers deposited. This opens the way to fabricate hollow microspheres with controlled wall thicknesses. Figures 23 and 24 show SEM micrographs of PBMA lattices coated with silicagel after calcination. Homogeneous shell coatings are produced on the PBMA lattices, and the coated particles maintain the spherical shape of the neat PBMA lattices. (Thermogravimetric analysis on samples confirms that the organic matter, i.e., colloidal core and bridging polymer, are removed during heating to 450°C.)

CONCLUSIONS

The present work demonstrates that it is possible to produce organic–inorganic nanocomposite and hollow microspheres, using emulsion polymerization followed by core removal by thermal means. This approach allows the fabrication of hollow microspheres (i) of tailored composition (inorganic or composites), and (ii) with predetermined diameters and size distribution (dependent on the colloidal template).

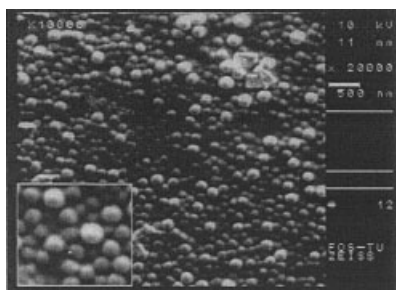**Figure 20** Photomicrograph of core particles after remaining in 100°C for 3 h.

Figure 21 Photomicrograph of core-shell particles with a layer of $CaCO_3$ after remaining in 100°C for 3 h.
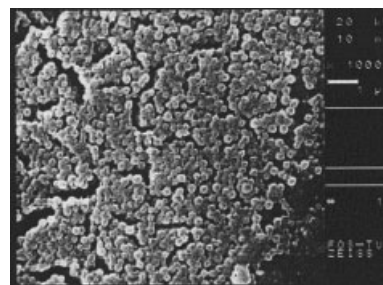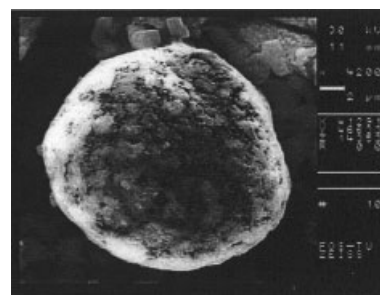

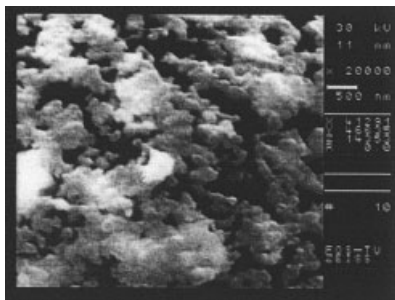**Figure 23** Photomicrograph of core-shell particles with a layer of silicagel after remaining in 500°C for 3 h.

Figure 24 Photomicrograph of core-shell particles with a layer of silicagel after remaining in 500°C for 3 h (zoom in Fig. 23).

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