Encapsulation of solid particles by the concentrated emulsion polymerization method

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The encapsulation of submicron sizes of alumina and fumed silica particles in crosslinked polyacrylamide is described. In a first step, a colloidal dispersion was prepared by dispersing the solid particles in an aqueous monomer (acrylamide) solution containing a water-soluble dispersant, a crosslinking agent, and a suitable initiator. In the second step, a concentrated emulsion was prepared at room temperature by dispersing the above colloidal system in decane containing a suitable surfactant, the volume fraction of the continuous phase being about 0.1. Upon heating at 40°C, polymerization of the dispersed phase of the gel-like emulsion obtained took place, thus encapsulating the solid particles in capsules with a polyhedral shape. Electron microscopy revealed that the solid particles were covered by polymer, and that the sizes of the capsules were around 4–5 μm for alumina and 1.0–1.5 μm for silica.

(Keywords: encapsulation; concentrated emulsion polymerization; solid particles)

INTRODUCTION

Encapsulation is a well known process in which tiny particles or droplets are covered by a coating or a membrane[1–6]. The role of encapsulation is either to isolate the active ingredient or to control the rate by which it leaves the capsule. As examples for the first case, one can mention the isolation of vitamins from oxygen or of a reactive core from chemical attack, and for the second case, the control of the rate of release of drugs or pesticides. A great many encapsulation techniques have been suggested and new ones are continually being developed. In encapsulation by coacervation[3], which is a phase separation phenomenon that occurs in colloidal systems, the coacervate layer is deposited uniformly around the individual particles of the active core material, which are uniformly dispersed in the medium. The capsules are provided with rigid walls by crosslinking the precipitated coacervates. Interfacial polymerization can also be used for encapsulation[4,5]. In this case, the active ingredient is dissolved or dispersed in an organic phase containing diacid chloride. The system thus obtained is dispersed in water containing a suitable surfactant. The instantaneous polymerization at the interface of each oil droplet by addition of diamine leads to the formation of a thin film enclosing the droplet containing the active ingredient. The encapsulation of inorganic powder by the soapless emulsion polymerization of methyl methacrylate in water in the presence of powders was also attempted[7,8]. Until now, most of the encapsulations of the active solid materials have been carried out for solids larger than 1 μm.

In the present paper, the concentrated emulsion polymerization method[9,10] is employed to encapsulate submicron inorganic powders. In the conventional emulsion polymerization, the volume fraction of the continuous phase is large, and polymerization occurs in micelles and the monomer molecules migrate from the monomer droplets to the micelles[11]. In contrast, in concentrated (gel-like) emulsion polymerization the volume fraction of the continuous phase is small (as small as 0.05), and polymerization occurs in the monomer cells of the dispersed phase[9]. The stability of this gel is ensured by the adsorption of a surfactant, which is dissolved in the continuous phase, on the interface of the droplets. In a concentrated emulsion, the dispersed phase consists of polyhedral cells separated by a network of thin layers of the continuous phase[10]. In a first step, a stable colloidal dispersion of the powder in an aqueous solution of a monomer containing an appropriate dispersant and a suitable initiator was prepared. This colloidal dispersion was subsequently employed as the dispersed phase of a concentrated emulsion whose continuous phase, decane, contained a surfactant. The role of the surfactant is to stabilize the gel-like concentrated emulsion. Upon heating at 40°C, polymerization took place and the solid particles were encapsulated in the polymer.

EXPERIMENTAL

Materials

Acrylamide (Polysciences) was purified by recrystallization in methanol. Potassium persulphate (Aldrich) was recrystallized from water. *N,N*-methylene bisacrylamide (Kodak), Sorbitane monooleate (Fluka), Triton X-45 (Rohm and Haas), decane (Fluka), and cyclohexane (Aldrich) were used as received. α-Alumina (M-300, 0.05 μm) and fumed silica (HS-5, $\sim 10^{-3}$ μm) were obtained from Metlade Corp. and Carbot Corp., respectively. Water was deionized and distilled.

Preparation of the capsules

A small amount of decane containing Sorbitane monooleate was placed in a 250 ml three-neck flask equipped with a mechanical stirrer, an addition funnel, and a

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nitrogen inlet. In addition, a colloidal dispersion was prepared by dispersing the solid powder in an aqueous solution of acrylamide, *N,N*-methylene bisacrylamide (crosslinking agent), and Triton X45 (dispersant) under stirring. Subsequently, potassium persulphate (initiator) was added to the system. The preparation of the concentrated emulsion was carried out at room temperature by dropwise addition of the colloidal dispersion to the continuous phase within about 10 min under a nitrogen atmosphere. Polymerization was carried out in a water bath at 40°C under a nitrogen stream for 6 h.

Electron microscopy

Scanning electron microscopy (SEM, Amray 100A) and transmission electron microscopy (TEM, Hitachi HS-8) were employed to examine the state of encapsulation of the powder. The polymerized gel was dispersed in cyclohexane to produce a latex solution. The specimens were prepared by placing a drop of the latex solution on carbon films coated copper grids for TEM and on a clean cover glass for SEM. The grids were allowed to dry before observation. In the case of SEM, a thin layer of gold was deposited prior to observation.

RESULTS AND DISCUSSION

The effect of a water-soluble dispersant on the stability of the colloidal dispersion is illustrated in *Figure 1*, which presents scanning electron micrographs of alumina powders dispersed in water in the absence and presence

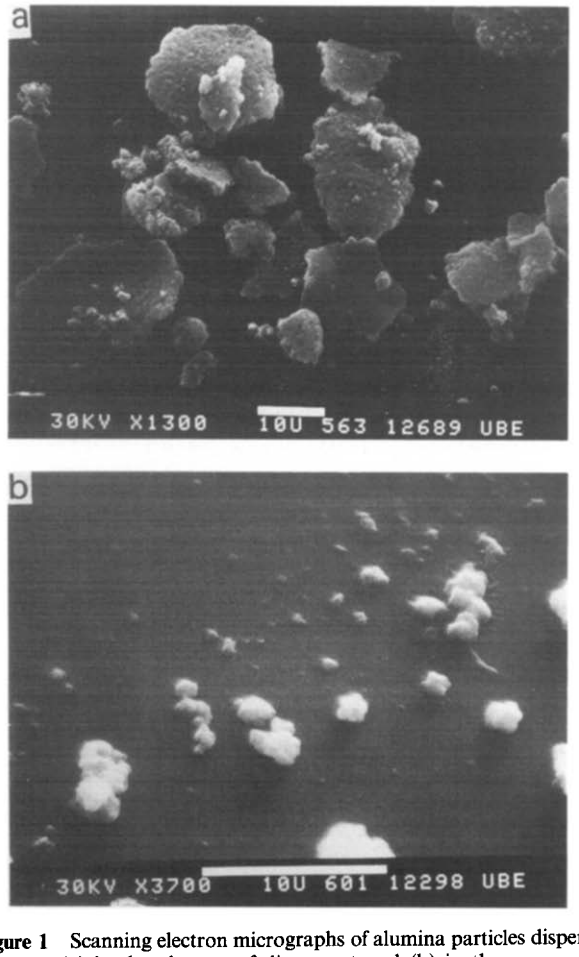

Figure 1 Scanning electron micrographs of alumina particles dispersed in water (a) in the absence of dispersant and (b) in the presence of dispersant

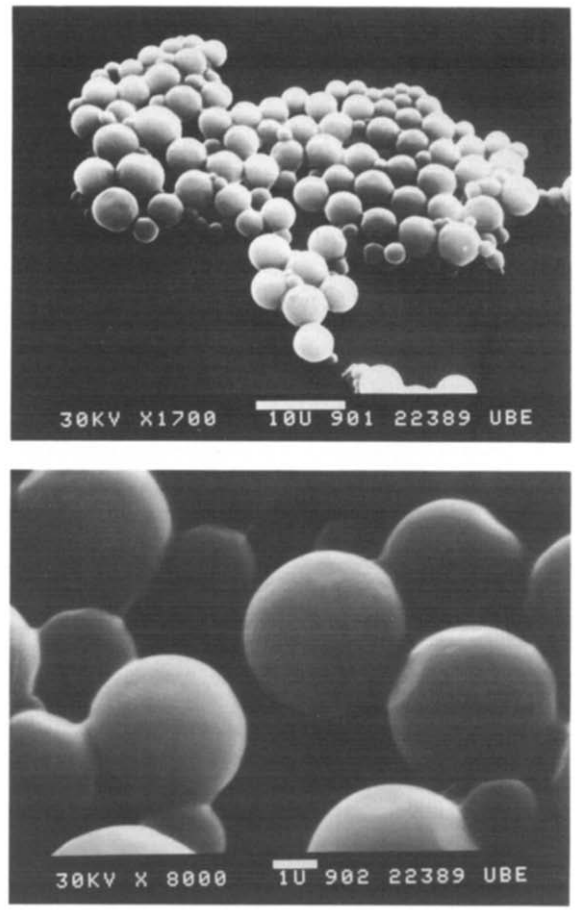

Figure 2 Scanning electron micrographs at two magnifications of crosslinked polyacrylamide latex particles with the composition PL1 (*Table 1*)

of dispersant. They show that the agglomeration of the solid particles decreases tremendously in the presence of the dispersant. The agglomerates are larger than 10 μm in the absence of dispersant and smaller by more than one order of magnitude in its presence. *Figure 2* presents scanning electron micrographs of crosslinked polyacrylamide latexes, free of solid particles, prepared by the concentrated emulsion polymerization method. The amounts of the components used in their preparation are listed in *Table 1* under PL1. The latexes have spherical shape and range in size from 1.0 to 4.0 μm. *Figure 3* shows scanning electron micrographs of latexes containing a water-soluble dispersant. The shape of the latexes is polygonal and their sizes are in the range of 0.5–3.0 μm. The amounts of various components involved are listed in *Table 1* under PL2. Scanning electron micrographs of latexes which contain a water-soluble dispersant and a smaller amount of polyacrylamide (PL3 in *Table 1*) are presented in *Figure 4*. The size of the latexes are in the range of 0.5–1.5 μm. By including a dispersant and decreasing the amount of polyacrylamide, the polymer latex particles became polygonal and smaller in size.

Figure 5 presents a scanning electron micrograph of a capsule, in which alumina particles are encapsulated in crosslinked polyacrylamide. *Table 2* lists under PLA1 the amounts of the components involved in the preparation of these capsules. The capsules have a polyhedral shape and their sizes are larger (around 5 μm) and more uniform than the polymer latexes free of solid particles. As reported before[10], the stability of the gel depends on

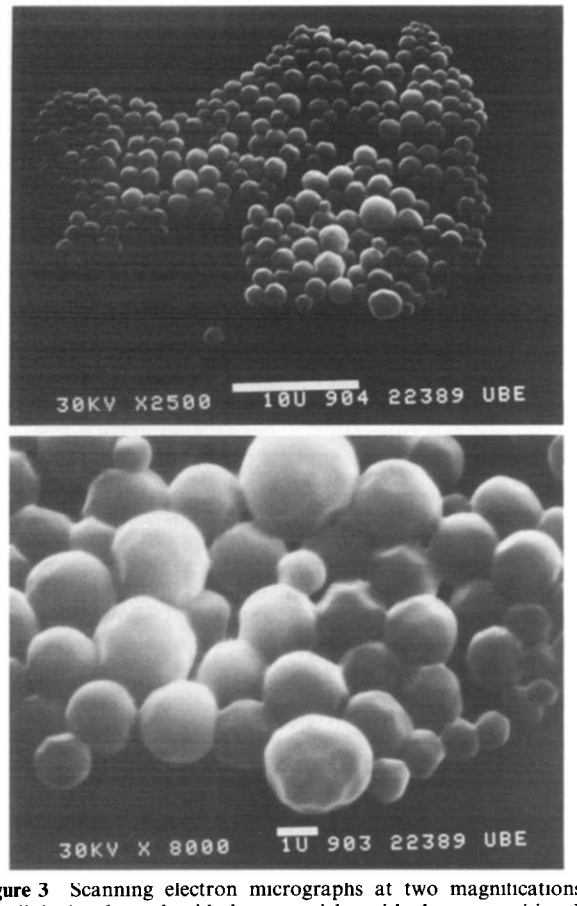

Figure 3 Scanning electron micrographs at two magnifications of crosslinked polyacrylamide latex particles with the composition PL2 (*Table 1*)

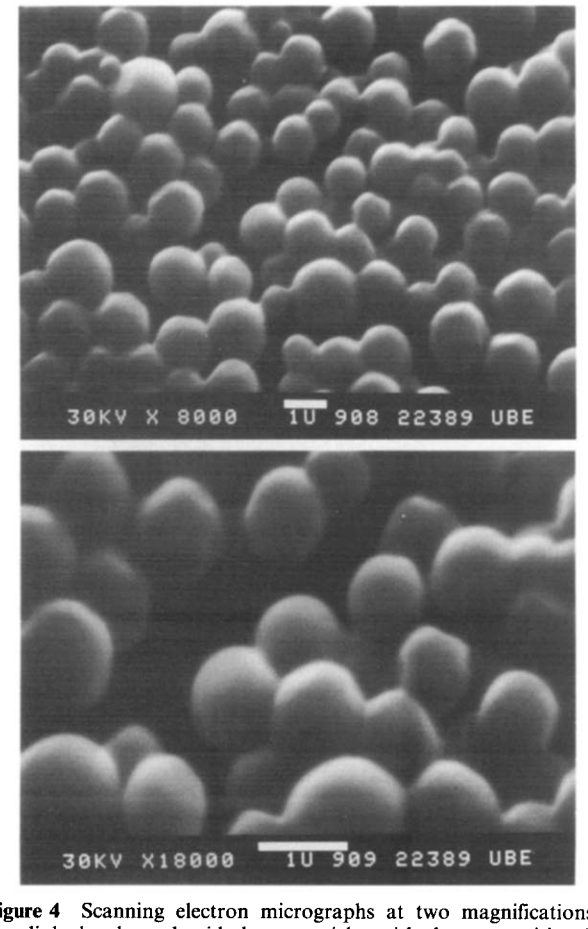

Figure 4 Scanning electron micrographs at two magnifications of crosslinked polyacrylamide latex particles with the composition PL3 (*Table 1*)

Table 1 Representative composition in the preparation of polyacrylamide latexes free of solid particles

	PL1	PL2	PL3
Dispersed phase			
Acrylamide (g)	5	5	2.5
Crosslinking agent (N,N-methylene bisacrylamide) (g)	0.5	0.5	0.25
Initiator (potassium persulphate) (g/g acrylamide)	0.01	0.01	0.01
Dispersant (Triton X-45) (g)	–	2	2
Water (g)	20	20	20
Continuous phase			
Decane (ml)	3	3	3
Surfactant (Sorbitane monooleate) (ml)	1.5	1.5	1.5

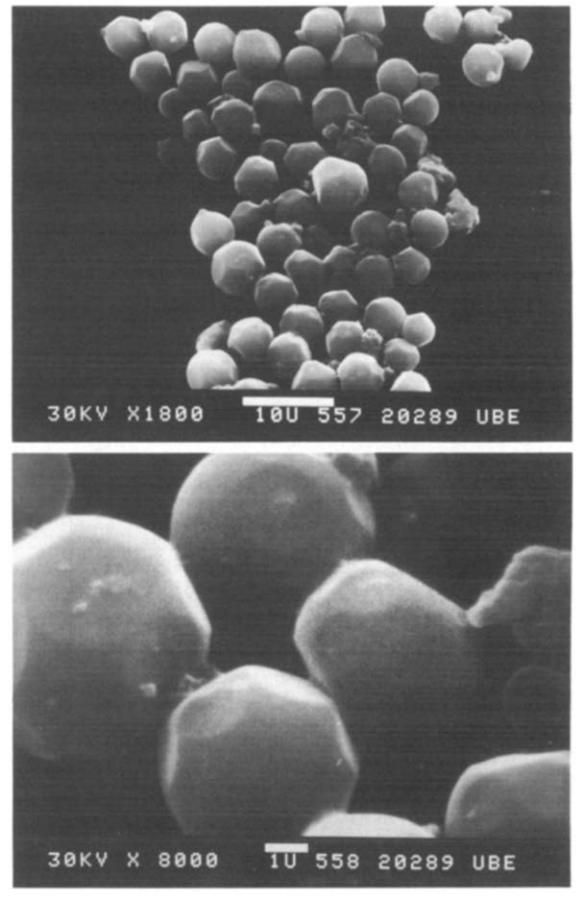

Figure 5 Scanning electron micrographs at two magnifications of capsules of alumina particles encapsulated in crosslinked polyacrylamide with the composition PLA1 (*Table 2*)

Table 2 Representative compositions in the preparation of alumina capsules

	PLA1	PLA2
Dispersed phase		
Acrylamide (g)	5	2.5
N,N-methylene bisacrylamide (g)	0.5	0.25
γ-alumina (g)	1.5	1.5
Dispersant (Triton X-45) (g)	2	2
Initiator (sodium persulphate) (g/g acrylamide)	0.01	0.01
Water (g)	20	20
Continuous phase		
Decane (ml)	3	3
Surfactant (Sorbitane monooleate) (ml)	1.5	1.5

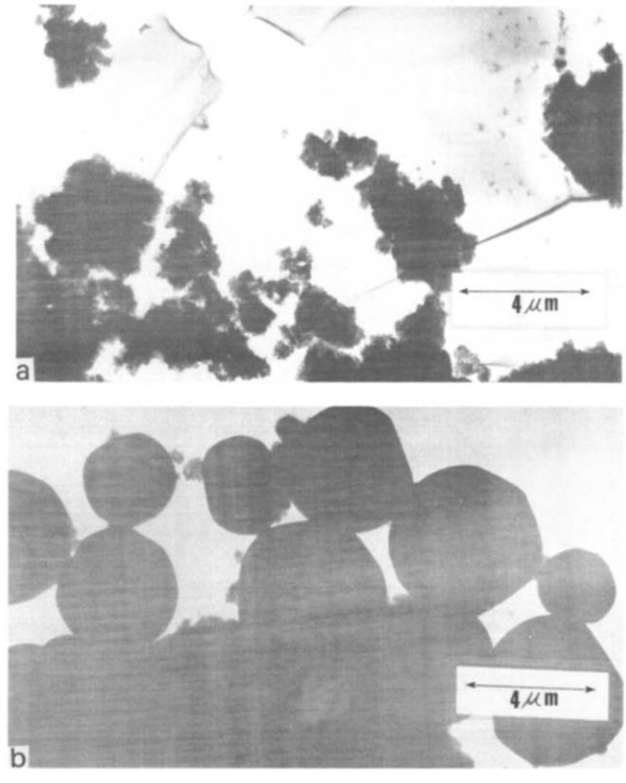

Figure 6 Transmission electron micrographs of (a) alumina and (b) alumina encapsulated in crosslinked polyacrylamide with the composition PLA1 (*Table 2*)

the polymerization temperature and the amount of acrylamide in the dispersed phase. Some of the cells of the gel coalesce during polymerization, forming bulk phases. As a result, some unencapsulated solid particles are observed. *Figures 6a* and *b* present transmission electron micrographs of alumina particles and capsules which contain alumina particles, respectively. The amounts of the components involved in the preparation of capsules are listed in *Table 2* under PLA1. *Figure 7* presents scanning electron micrographs of PLA2 capsules (*Table 2*), in which the amount of polymer is smaller than for PLA1. The size of the capsules is slightly smaller, and their shape is changed (perhaps because of the loss of water?).

Very fine solid particles, namely, fumed silica, were also encapsulated by the concentrated emulsion polymerization method. *Figure 8* shows scanning electron micrographs of silica capsules, in which fumed silica particles are encapsulated in crosslinked polyacrylamide. The amounts of the components involved are listed under PLS1 in *Table 3*. The PLS1 capsules range from 1.0 to 1.5 μm. These capsules also have polyhedral shape and are slightly smaller than the PL3 polymer latex particles. Some unencapsulated particles have been observed because of the coalescence during polymerization of some cells of the gel.

CONCLUSIONS

Three steps are employed in the encapsulation process. The first involves the preparation of a stable colloidal

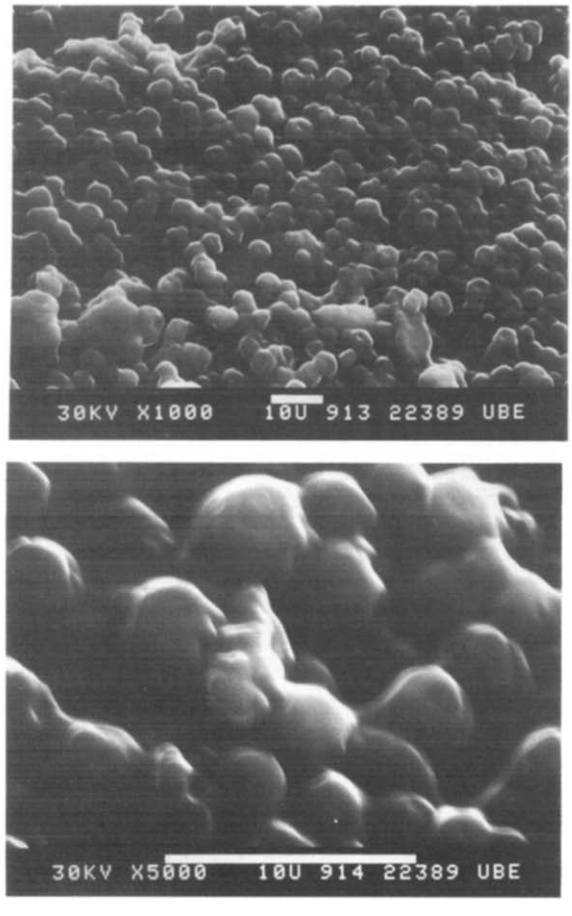

Figure 7 Scanning electron micrographs at two magnifications of alumina encapsulated in crosslinked polyacrylamide with the composition PLA2 (*Table 2*)

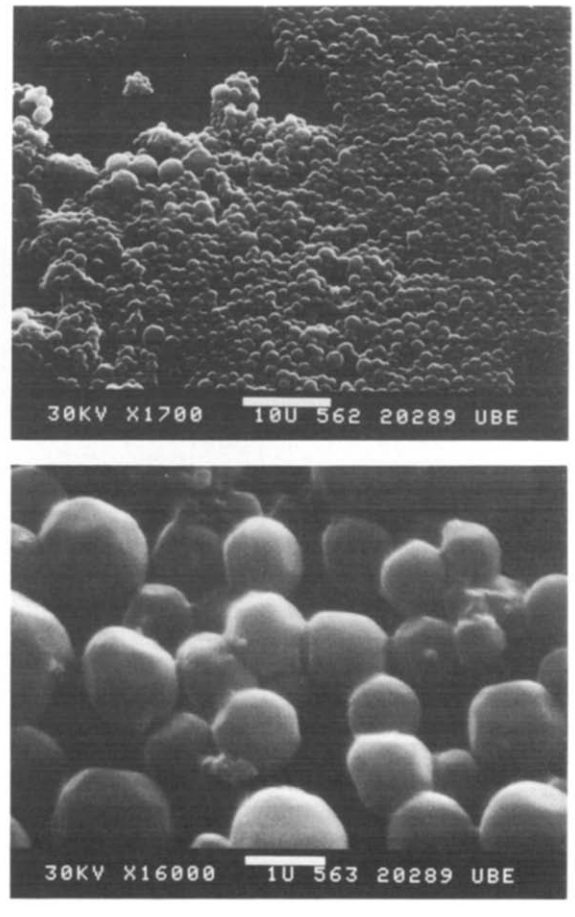

Figure 8 Scanning electron micrographs at two magnifications of fumed silica encapsulated in crosslinked polyacrylamide with the composition PLS1 (*Table 3*)

Table 3 Representative compositions in the preparation of silica capsules

	PLS1
Dispersed phase	
Acrylamide (g)	5
N,*N*-methylene bisacrylamide (g)	0.5
Fumed silica (g)	0.75
Dispersant (Triton X-45) (g)	2
Initiator (sodium persulphate) (g/g acrylamide)	0.01
Water (g)	20
Continuous phase	
Decane (ml)	3
Surfactant (Sorbitane monooleate) (ml)	1.5

dispersion of solid particles in an aqueous solution of a monomer that contains a crosslinking agent, an initiator and a water-soluble dispersant. In the second step, the colloidal dispersion is used as the dispersed phase in the preparation at room temperature of a concentrated, gel-like emulsion having decane containing a surfactant as the continuous phase. Finally, the system is polymerized *in situ* at 40°C to produce capsules containing particles.

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