Macromol. Symp. ***151,*** *377–385 (2000)*

Silica-Polystyrene Composite Particles

Elodie Bourgeat-Lami*, Jacques Lang[1]

LCPP, Bât. 308F, BP 2077, 43 Bd. du 11 Novembre. 1918, 69616 Villeurbanne, France. [1]Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg, France

SUMMARY: The synthesis of silica-polystyrene composite particles by dispersion polymerization of styrene in a mixture of ethanol and water is described. The silica beads are modified before polymerization using the 3-(trimethoxysilyl)propyl methacrylate coupling agent. Composite particles with different shapes and different numbers of silica beads are obtained. The evolution of the shape and composition of the composite particles is studied as a function of three main parameters, namely, the silica beads size and concentration, the solvent composition and the nature or amount of stabilizer.

Introduction

Composite latexes are particles made of at least two different polymeric components. Such composite materials enter in a wide variety of industrial applications since it is of great interest to produce materials that combine different properties; for instance mechanical strength given by the core and compatibility with the surrounding medium given by the shell. In the last years, attempts to obtain such synergistic effects have been largely developed with the incorporation of fillers into polymers and the synthesis of hybrid organic-inorganic materials [1-5]. The interest in such systems stems from their promising mechanical, optical or structural properties which are much dependent on the composition and on the morphology of the composite particles which, in turn, are greatly affected by the synthesis conditions. It is our goal in the present work to report a new route for the synthesis of organic-inorganic composite particles and to describe how it is possible to control the particle morphology by simply changing the polymerization conditions. We hope that this kind of study will also help to understand the mechanism by which such composite particles are obtained.

Materials and methods

Reagents Absolute ethanol, ammonium hydroxyde, tetraethyl orthosilicate (TEOS), 3-(trimethoxysilyl)propyl methacrylate (MPS), the monomer, styrene, the initiator, 2,2'-azobis (isobutyronitrile) (AIBN), and the poly (N-vinylpyrrolidone) (PVP K30) stabilizer have the

CCC 1022-1360/00/$ 17.50+.50/0

same origin as that given in previous works [6-7]. The poly (styrene-b-ethylene oxide) diblock copolymer (PS/PEO, 3000/3000) was purchased from Goldschmidt S.A. and used as received.

Synthesis, modification and characterization of the silica sols Colloidal amorphous silica dispersions in aqueous ammoniacal ethanol were prepared by the Stöber method [8]. Coating of the bare silica particles was performed by addition, directly in the medium of an excess of the 3-(trimethoxysilyl)propyl methacrylate (MPS) coupling agent. The dispersions of MPS coated silica beads were dialyzed against ethanol solutions to remove any unreacted MPS and ammonia. MPS coated silica sols with different amounts of water and the same silica concentrations were prepared from at least five centrifugations/redispersions in the medium with the desired water composition. The grafted silica sols were characterized by elemental analysis, fourier transformed infrared and solid state NMR spectroscopies [6]. Particle sizes were determined by transmission electron microscopy (TEM) using a Philips CM12 electron microscope. Highly diluted dispersion was cast on a carbon coated cooper grid and allowed to air dry. Diameters were determined on the TEM micrographs from a large number of particles.

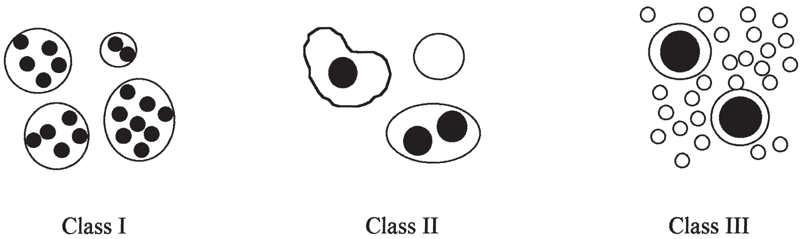
Synthesis and characterization of the composite silica-polystyrene colloids In a typical run, the dialyzed modified alcosol of given composition was introduced in a 250 ml reactor fitted with a condenser. Known amounts of stabilizer were dissolved into the reaction medium under nitrogen atmosphere and stirring. After air degassing, styrene monomer along with the initiator was added at once at 60°C. Polymerization was carried out for 24 hours for complete reaction. Particle diameters were determined by TEM.

Evidence of polymer bonding at the silica-polystyrene composite interphase

In contrast to parent silica, which is hydrophilic and charge stabilized, the MPS coated silica particles are hydrophobic and give rise to colloidal stable iridescent dispersions in ethanol-toluene mixtures. We have chosen methacryloxypropyl functionalized silica since the organophilic character of the grafted surface can enhance the adsorption of monomer and/or polymer on the mineral surface and the reactivity of the coupling agent in free radical polymerization reactions allows the covalent grafting of polymer at the silica surface. That grafting takes place is evidenced by several techniques described in a previous work [6]. We demonstrated that the formation of tightly bonded polystyrene at the silica surface allows encapsulation of the silica beads with the whole synthesized polymer. Modification of the silica surface appeared absolutely necessary to obtain true composite particles with silica beads embedded into polymer. Indeed, as shown by several microscopy techniques [6], when un-grafted silica particles are used in the dispersion polymerization, polymer particles separated from the silica beads are obtained.

Morphology of the Composite Particles

For each sample, the morphology of the composite particles is checked by TEM. The term morphology is used to describe both the shape and composition of the composite particles. By ***shape,*** we mean the external contour of the composites. Some of the particles exhibit spherical shapes whereas some others have more distorted irregular shapes. In addition to changes in shape, the composite particles are characterized by their ***composition,*** i.e., by the average number, N_s, of silica beads they contain. However, since in some cases latex particles without silica are also present after polymerization, we define the average number, N_a, of silica beads per particle which corresponds to the ratio of the number of silica beads over the total number of latex particles (particles with and without silica). N_a values lower than one indicate the presence of free latex particles, i.e., latex particles that do not contain silica, while high N_a values correspond to composite particles containing a large number of silica beads. Notice that we never observed free silica beads in the composite latexes which means that each of the silica beads introduced in the polymerization medium ends up with polymer on their surface. Examples of typical shapes and compositions encountered in the present work are given in Scheme 1 and illustrated by Figure 1.



Scheme 1. Schematic representation of the different classes of morphologies for the composite particles (the black circles represent the silica beads).

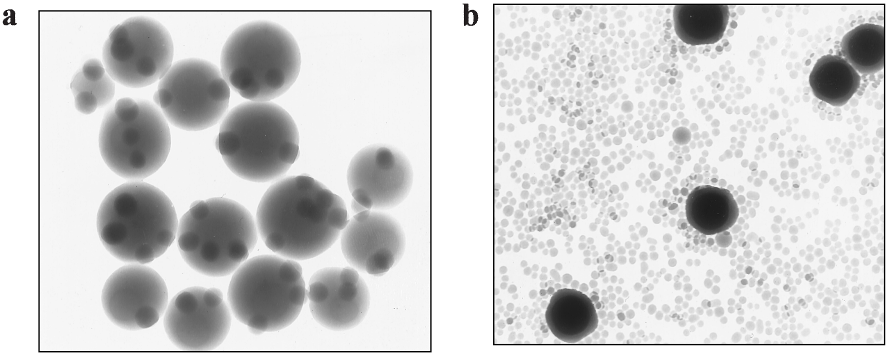


Figure 1: TEM micrographs of silica-polystyrene composite particles: (a) sample C4 in Table 1, and (b) sample C19 in Table 3.

Class I and Class II correspond to composite particles synthesized in presence of the PVP K30 stabilizer, whereas Class III corresponds to composite particles obtained with the PS/PEO block copolymer stabilizer.

Three methods were used for the determination of N_a.

(1) When the composite particles have a spherical shape and when no free latex particles are present (Class I in Scheme 1), N_a can be expressed as a function of the average diameters D_p (SiO_2) and D_p (Composite) of the silica beads and the composite particles, respectively, as:

$$Na = \frac{1}{\left(d_{SiO2} \times w + 1\right)} \times \left[\frac{Dp\ (Composite)}{Dp\ (SiO_2)}\right]^3 \qquad (1)$$

where w is the weight ratio of synthesized polymer to silica, d_{SiO_2} is the density of silica equal to 1.8 g/cm^3, and the density of polymer is assumed equal to 1.

(2) For non spherical composite particles, where it is not possible to measure D_p (Composite) (Class II in Scheme 1), N_a is determined by counting directly on the TEM micrographs the number N_i ($i = 0$ to 4) of particles that contain 0, 1, 2, 3 and 4 silica beads. From the values of N_i, measured over a large number of particles, one can deduce an average number of silica beads per particle defined as:

$$Na = \sum_{i=0}^{4} iN_i \Big/ \sum_{i=0}^{4} N_i \qquad (2)$$

(3) When there are too many free latex particles to be counted accurately and when all the composite particles are spherical and contain only one silica bead (Class III in Scheme 1), one can determine by TEM the diameter of the silica beads, D_p (SiO_2), of the encapsulated silica,

D_p (Composite), and of the free latex particles, D_p (Free latex), respectively, and deduce the average number N_a, as a function of w and d $_{SiO_2}$, from the relation:

$$Na = \left[\frac{[Dp\ (\text{Free latex})]^3}{[Dp\ (\text{Free latex})]^3 - [Dp\ (\text{Composite})]^3 + (d_{SiO_2} \times w + 1) \times [Dp\ (SiO_2)]^3} \right] \quad (3)$$

Influence of the size and concentration of the silica beads

By changing the size or concentration of the silica beads, one changes the number, N_p SiO_2, of silica beads in the dispersion medium. Table 1 illustrates the relation between the composition of the composite particles and the number, N_p SiO_2, of silica beads, when PVP K30 is used as stabilizer. The values in Table 1 indicate that when decreasing the number of silica particles in the polymerization medium, the number, N_0, of free latex particles increases whereas the number of composite particles with more than one silica beads decreases which contributes to a decrease in the average number, N_a, of silica beads per particle.

Table 1. Number, N_i [a], of particles with i silica beads and average number, N_a, of silica beads per particles as a function of the number, N_p SiO_2, of silica beads.

Sample	Class	D_p SiO_2 (nm)	SiO_2 (g)	N_p SiO_2 [b]	N_0	N_1	N_2	N_3	N_4	$N_{>4}$	N_a	N_p total [c]
C1	I	13	1.5	$6.0\ 10^{17}$	0	0	0	0	0	100	3158 [d]	$1.9\ 10^{14}$
C2	I	72	1.5	$4.3\ 10^{15}$	0	2	2	4	6	86	23 [d]	$1.8\ 10^{14}$
C3	I	49	0.3	$2.7\ 10^{15}$	0	0	0	2	2	96	22 [d]	$1.2\ 10^{14}$
C4	I	120	1.5	$9.2\ 10^{14}$	0	8	19	25	19	29	4 [d]	$2.3\ 10^{14}$
C5	/	191	3	$4.6\ 10^{14}$	0	50	31	9	6	4	/	/
C6	/	191	1.5	$2.3\ 10^{14}$	0	54	23	8	8	7	/	/
C7	II	352	1.5	$3.7\ 10^{13}$	0	73	23	4	0	0	1.3 [e]	$2.8\ 10^{13}$
C8	II	191	0.2	$3.1\ 10^{13}$	3	94	3	0	0	0	1 [e]	$3.1\ 10^{13}$
C9	II	558	1.5	$9.2\ 10^{12}$	8	78	8	6	0	0	1.1 [e]	$8.3\ 10^{12}$
C10	II	629	1.5	$6.4\ 10^{12}$	26	70	3	1	0	0	0.8 [e]	$8.0\ 10^{12}$
C11	II	629	1	$4.3\ 10^{12}$	42	50	6	1	1	0	0.7 [e]	$1.0\ 10^{13}$
C12	II	558	0.5	$3.1\ 10^{12}$	59	41	0	0	0	0	0.4 [e]	$7.8\ 10^{12}$
C13	II	629	0.15	$6.4\ 10^{11}$	95	5	0	0	0	0	0.05 [e]	$1.3\ 10^{13}$

Polymerization was performed under the following conditions: ethanol, 94.5g; water, 5.5g; total solvent, 100g; PVP K30, 2g; AIBN, 0.1g; Styrene, 10g.

[a] Relative to a total number of 100 particles. The real number of particles used for the counting was between 50 and 200 - [b] Per 100g of solvent, calculated from D_p SiO_2 (nm) and SiO_2 (g) - [c] Per 100g of solvent, calculated from N_p SiO_2 and N_a - [d] Calculated with Eq. (1) - [e] Calculated with Eq. (2)

In addition to changes in the composition of the composite particles, one observes on the TEM micrographs, changes of their shape. Larger is the silica particle size and higher the volume fraction of the silica beads into the composite particles, the more distorted is the shape of the composite.

Solvent composition effects

For given silica particle size and concentration, the composition of the composite particles is also largely dependent on the amount of water contained in the solvent. The results in Table 2 indicate that the larger the amount of water, the lower is the value of N_a.

Table 2. Number, N_i^a, of particles with i silica beads and average number, N_a, of silica beads per particles as a function of the solvent composition.

Sample	Class	EtOH (g)	Water (g)	N_0	N_1	N_2	N_3	N_4	$N_{>4}$	N_a	N_p total [b]
C14	II	94.5	5.5	0	8	19	25	19	29	4 [c]	$3.2\ 10^{14}$
C15	II	85	15	0	92	7	1	0	0	1.1 [c]	$1.1\ 10^{15}$

Polymerization was performed under the following conditions: silica (D_p = 108 nm), 1.5g; total solvent, 100g; PVP K30, 2g; AIBN, 0.1g; Styrene, 10g

[a] Relative to 100 particles - [b] Per 100 g of solvent, calculated from N_p SiO_2 and N_a - [c] Calculated with Eq. (2)

Influence of the nature and concentration of the stabilizer

To illustrate the role of stabilization in the mechanism of formation of the composite particles, we chose a stabilizer with a completely different stabilizing efficiency, i.e., a preformed amphiphilic poly (styrene-b-ethylene oxide) block copolymer (PS/PEO). Table 3 shows that drastic changes in the composition of the composite particles appear when PVP is replaced by the copolymer PS/PEO as stabilizer. N_a is greatly reduced which means that a large number of free latex particles is obtained. At the same time, the shape of the composites is modified and a core-shell morphology is found for the encapsulated silica (Class III in Scheme 1). Table 3 also shows that it is possible to increase N_a by simply decreasing the amount of stabilizer in the polymerization medium.

Table 3. Number, N_i^a, of particles with i silica beads and average number, N_a, of silica beads per particles as a function of the nature and concentration of the stabilizer.

Sample	Class	Stabilizer (g)		N_0	N_1	N_2	N_3	N_4	$N_{>4}$	N_a	N_p total [b]
C18	II	PVPK30	2	0	8	19	25	19	29	4 [c]	$3.2\ 10^{14}$
C19	III	PS/PEO	2	97	3	0	0	0	0	0.03 [d]	$4.2\ 10^{16}$
C20	III	PS/PEO	1	94	6	0	0	0	0	0.06 [d]	$2.1\ 10^{16}$
C21	III	PS/PEO	0.5	57	43	0	0	0	0	0.43 [d]	$2.9\ 10^{15}$

Polymerization was performed under the following conditions: silica (D_p = 108 nm), 1.5g; ethanol, 94.5g; water, 5.5g, total solvent, 100g; AIBN, 0.1g; Styrene, 10g

[a] Relative to a total number of 100 particles - [b] Per 100 g of solvent, calculated from N_p SiO_2 and N_a

[c] Calculated with Eq. (2) - [d] Calculated with Eq. (3)

Discussion

It is known that in dispersion polymerization one of the determining parameters which govern in particular the size of the latex particles are the solvent composition, and the nature and concentration of the stabilizer [9]. By increasing for instance the amount of water in the polymerization medium, or the stabilizer concentration, one decreases the onset at which the polymer particles precipitate and one increases the final particles number. In the present study, we have deliberately changed the experimental conditions in order to influence significantly the mechanism by which the polymer is formed. Indeed, it clearly appears from the above results that the overall number, N_p total, of particles (free polymer and composite latex particles) synthesized in the different experimental conditions depicted in Tables 1-3, does not depend much on the size or concentration of the silica beads but depends rather on the polymerization conditions, as for instance the presence of water or the nature and concentration of the stabilizer. Indeed, the values in Table 1 show that the total particle number is constant in class I and in class II, while the number of silica beads into the polymerization medium decreases by a factor 1000 in class I, and a factor 100 in class II. On the other hand, the overall number of particles increases from around 10^{14} to around 10^{16} when using the block copolymer PS/PEO stabilizer instead of PVP, meanwhile the number of silica beads into the polymerization medium is maintained constant (samples C18 and C19 in Table 3). These results indicate that the silica beads do not act simply as a seed for encapsulation. In addition, whatever the size or the concentration of the silica beads, we have shown, as a part of this work, that the overall number of particles obtained in presence of the silica beads is of the same order of magnitude as that obtained in the absence of silica into the polymerization medium (blank experiment).

So, from a macroscopic point of view, the synthesis seems to proceed as if there were no silica beads into the medium, indicating that it is essentially the parameters of the polymerization reaction which govern the formation of the composite particles rather than the silica beads. The average number, N_a, of silica beads per particle is then controlled by the relative number of silica beads used in the synthesis and of latex particles obtained in the blank experiments. N_a is larger than one when the number, N_p SiO_2, of silica beads is larger than the number, N_p (blank), of latex particles (case of class I in Table 1). With PVP, the diameter of the latex particles in the blank is around 800 nm, which corresponds to a relatively low number of particles. N_a is close to or lower than one when N_p SiO_2 is equal or lower than N_p (blank). This is obtained either by decreasing the number of silica beads (case of class II in Table 1), or by increasing the number of polymer particles in the blank (case of class II in Table 2 and of class III in Table 3). In one side, addition of water decreases the size of the latex particles from 800 nm to 500 nm and, on the other side, the PS/PEO stabilizer gives rise to low latex particles sizes (60 nm). In both cases N_p (blank) increases which produces a decrease of N_a.

Conclusion

A variety of silica-polystyrene composite particles has been obtained by dispersion polymerization, by changing the nature of the stabilizer, the composition of the solvent, and the size and concentration of the silica beads. The morphologies obtained include composite particles containing a great number of silica beads, as well as very regular core-shell particles. One of the main results is that the morphology of the composite particles is governed by the size of the latex particles formed in the blank, i.e., in the absence of silica. When PVP is used as stabilizer, large latex particles are obtained in the blank and, with a number of silica beads in the reaction medium higher than the number of blank polymer, composite particles with a great number of silica beads are formed. When the block copolymer PS/PEO is used as stabilizer, latex particles much smaller than those obtained with PVP, are formed in the blank. In this case, each composite particle contains only one silica bead surrounded by a shell of polystyrene. Latex particles, which do not contain silica beads, are also present, but they can be easily separated from the composite particles by centrifugation [10]. This work describes a new method for the synthesis of composite particles. One of the advantage of the dispersion polymerization method employed here, is that the synthesis of the composite particles is undertaken in the same solvent, namely a mixture of ethanol and water, than the one used for the synthesis of the silica beads and for the grafting of the coupling agent, MPS.

References

1. *"Hybrid Organic-Inorganic Composites"*, J. E. Mark, C. Y-C. Lee and P. A. Bianconi (Eds.), American Chemical Society Symposium Series 585, Washington DC 1995
2. H.F. Zirkzee, *Ph. D. Thesis, A novel approach to the encapsulation of silica particles*, Eindhoven, The Netherlands, 1997
3. A. M. van Herk, A. L. German, in: "*Microspheres Microcapsules & Liposomes, Vol. 1, Preparation & Chemical Applications"*, R. Arshady (Ed.), Citus Books, London 1999, chap. 17, p. 457-486
4. C. L. Huang, E. Matijevic, J. Mater. Res. **10**, 1327 (1995)
5. C. Barthet, A. J. Hickey, D. B. Cairns and S. P. Armes, Adv. Mater. **11**, 408-410 (1999)
6. E. Bourgeat-Lami, J. Lang, J. Colloid Interface Sci. **197**, 293-308 (1998)
7. E. Bourgeat-Lami, J. Lang, J. Colloid Interface Sci. **210**, 281-289 (1999)
8. W. Stöber, A. Fink and E. Bohn, J. Colloid Interface Sci. **26**, 62 (1968)
9. "Dispersion Polymerization in Organic Media", K. E. J. Barret (Ed.), Wiley, London 1975
10. F. Corcos, E. Bourgeat-Lami, C. Novat and J. Lang, To appear in *Colloid and Polymer Science*