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Poly(ethyl acrylate) latexes encapsulating nanoparticles of silica : 1. Functionalization and dispersion of silica

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Silica (Aerosil A200V) has been functionalized by reaction with methacryloylpropyltrimethoxysilane (MPTMS) in toluene. The grafting yield first increases with the ratio MPTMS/SiOH and then levels off after full monolayer coverage, each molecule of MPTMS covering 71 Å^2. A greater amount can be grafted if the MPTMS is first hydrolysed and partly condensed, and then reacted with the silica. A high degree of functionalization is needed to get complete dispersion of the silica in toluene. The redispersion of the functionalized silica in water is difficult; the best results are obtained in the presence of isobutanol as dispersing agent, after three days of treatment at pH 9.5, which causes the hydrolysis of the remaining methoxy groups.

(Keywords: encapsulated silica; surface functionalization; dispersion in water)

INTRODUCTION

A number of applications exist for polymer-encapsulated particles: Improved mechanical properties of filler-reinforced rubbers are obtained when there is an interfacial bond between the matrix and the filler. The pigments used in cosmetics, inks and paints are better dispersed, and confer better performance, when they are encapsulated with a polymer layer compatible with the binder. Magnetically responsive particles covered with functionalizable polymers are of special interest in biotechnological applications.

Among the various methods of encapsulation, emulsion polymerization is gaining importance. Surfactant-free emulsion polymerizations have been carried out in the presence of many inorganic particles such as oxides, metal powders, glass, graphite and $CaCO_3$ (refs 1–6). It appears that in most cases the inorganic particles are covered with polymer particles strongly fixed mainly through electrostatic forces. Similar charge effects, modulated by pH, were reported by Haga *et al.*[7] for the surfactant-free emulsion polymerization of methyl methacrylate (MMA) or styrene on TiO_2. The same authors reported interesting light-sensitive effects of zinc oxide and cadmium sulfide encapsulated in the same way [8–10]. The surfactant-free emulsion polymerization of vinyl acetate in the presence of small quartz particles was described and modelled by Hergerth and Schumultzer[11–13], showing that oligomers are initially adsorbed on the surface of the particle, where they form a layer in which further polymerization takes place. When the surface area offered by the quartz is high enough, there is no formation of pure polymer particles. The importance of the hydrophobic layer initially formed during the process on the surface of activated (ground) particles has also been recognized by Hasegawa[14]. A variety of methods can be used to introduce the hydrophobic layers: for instance nonionic surfactants [15], amphiphilic polymers[16] or simply hydroxypropyl cellulose[17]. An organophilic bilayer of surfactant at the surface of pigments has allowed polymerization of styrene at this surface[18].

However, in all the above methods, desorption of the polymer covering the particles can easily occur when the conditions of pH and ionic strength are changed. More stable encapsulations can be obtained in at least two different ways. One is based on a two-step process involving inverse emulsion polymerization of a water dispersion of the inorganic particle (iron oxide) in a water solution of acrylamide and a small amount of a crosslinker, ethylenebisacrylamide; the inverse latex obtained is then inverted in water[19]. The second method consists of using a coupling agent containing a double bond or an initiator moiety. This method has been followed by Caris *et al.*[20] with TiO_2 modified with a functional titanate coupling agent, and extended more recently by the same group for styrene polymerization[21]. Silane coupling agents have also been used either by first treating the inorganic surface—which has been done by Hagi and Oonaka with octadecyltriethoxysilane[22]—or directly with a mixture of a silane initiator, monomers and inorganic particles[23]. A rather old patent by Union Carbide describes many of these methods[24].

However, in most of the literature studies, neither the dispersion state of the inorganic particles nor the effectiveness of the encapsulation were described in

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detail. So we have decided to carry out a study beginning with the chemical modification of the surface with a reactive silane coupling agent in order to obtain covalent grafting of at least a part of the polymer during the emulsion polymerization. Silica was chosen as a model for the inorganic particle, and the coupling agent was methacryloylpropyltrimethoxysilane (MPTMS) carrying a polymerizable group linked to the silicon atom through a non-hydrolysable Si–C bond. In this first paper we describe the chemical modification of the silica with the coupling agent and the dispersion process used before the emulsion polymerization. The grafting process of ethyl acrylate polymers will be the subject of the second paper, while the third one will be devoted to the study of the morphology of films prepared from these grafted latexes and their outstanding mechanical properties[25]. A preliminary study allowed us to select the monomer and the surfactants[26] as well as the polymerization conditions which give good encapsulation[27].

EXPERIMENTAL

Materials

Non-porous silica particles (Aerosil A200 V, Degussa), with an average diameter of 12 nm and a specific area of 228 m^2 g^{-1}, were used. For characterization of the surface SiOH groups, the silica was first dried at 450°C for hours. The number of hydroxyl groups at the silica surface has been determined by measuring the pressure of ethane evolved from the reaction of triethylaluminium (TEA) with surface silanol groups[28]. The surface silanol content before grafting was found to be 6 μmol m^{-2}.

The methacryloylpropyltrimethoxysilane (MPTMS) coupling agent was purchased from Fluka and used as received. MPTMS hydrolysis was performed under acidic conditions by adding acidic water (HCl, pH = 2) to a mixture of MPTMS in dry deuterated methanol. The molar ratios were 2 for MeOH/MPTMS and 3 for H_2O/MPTMS. Hydrolysis was followed by ^1H n.m.r. using a Bruker AC250 spectrometer.

Toluene (from SDS) was distilled over activated molecular sieves under a nitrogen atmosphere before use. Isobutanol, sodium dodecyl sulfate and sodium ethylhexyl sulfosuccinate were used as supplied.

Functionalization

Grafting has been carried out in dry toluene (120 ml) at reflux temperature under a N_2 atmosphere. Dried silica (5 g) was first suspended in the organic medium and, after addition of controlled amounts of MPTMS (0.15 to 2.4 g), the mixture was stirred overnight.

For chemical analysis, grafted silica was recovered by centrifugation, washed three times with toluene to remove excess MPTMS and finally dried under vacuum overnight at 80°C.

Characterization

The carbon content C was determined by elemental analysis. It can be used to calculate the actual coverage of the silica surface by the MPTMS, according to the Berendsen equation[29]:

$$\text{coverage } (\mu\text{mol m}^{-2}) = 10^6 C/[1200\, N_c - C(M-1)] \times S$$

where N_c is the number of carbon atoms in the grafted silane molecule, M is the molar mass of the silane and S is the specific area of the silica (m^2 g^{-1}).

A Bruker AM250 spectrometer was used to obtain the ^{29}Si and ^{13}C cross-polarization/magic-angle spinning (CP/MAS) solid-state n.m.r. spectra, working at 39.7 and 50.3 MHz respectively.

Particle size and particle-size distribution were obtained from dynamic light scattering (quasi-elastic light scattering, q.e.l.s.) with a Brookhaven instrument.

RESULTS AND DISCUSSION

Grafting methacryloylpropyltrimethoxysilane onto silica

The functionalization studies were first carried out in toluene solution. The concentrations of MPTMS have been calculated by reference to the amount of silanol groups available (6.0 μmol m^{-2} or 1.37 meq g^{-1}). A large range below and above the stoichiometry of one mole MPTMS per mole of SiOH groups was investigated. The data are reported in *Table 1*; the grafting yield, from the amount of C given by elemental analysis, is calculated using the Berendsen formula, assuming the formation of one Si–O–Si bond per MPTMS grafted. The data of *Table 1* clearly show that the amount grafted increases with increasing amount of MPTMS used, up to the amount corresponding to the stoichiometry, and then levels off. However, the maximum yield corresponds to less than the stoichiometry. The maximum average number of MPTMS molecules grafted corresponds to less than 40% of the silanol groups reacted. There are about 2.6 silanol groups per molecule of MPTMS.

There are two possible reasons for such a limitation. First, it is known that a trialkoxysilane coupling agent can be easily grafted to two vicinal Si–OH groups. The reaction of three methoxy groups of the same silane molecule is considered as a much less probable event. Some qualitative information about the distribution of these grafting reactions can be obtained from ^{29}Si n.m.r.

Table 1 Data of grafting methacryloylpropyltrimethoxysilane (MPTMS) onto silica[a]

Amount of MPTMS (g)	Ratio $\frac{\text{MPTMS}}{\text{SiOH}}$	Theoretical coverage (μmol m^{-2})	C (%)	Actual coverage (μmol m^{-2})	Grafting yield (%)
0.15	0.092	0.55	1.54	0.87	100
0.30	0.18	1.08	1.99	1.14	100
0.43	0.26	1.57	3.01	1.79	100
0.60	0.37	2.20	2.90	1.71	78
0.75	0.45	2.70	2.90	1.71	63.5
1.00	0.60	3.60	3.15	1.88	52
1.24	0.76	4.55	3.14	1.87	41
1.50	0.92	5.50	3.07	1.83	33.3
1.75	1.07	6.40	3.85	2.35	36.7
1.82	1.12	6.70	4.15	2.33	34.8
1.90	1.16	6.96	3.83	2.33	33.5
2.38	1.45	8.73	3.77	2.29	26.3

[a] The ratio MPTMS/SiOH is the mole ratio between the amount of MPTMS engaged and the amount of Si–OH groups on the silica surface. It allows one to calculate the theoretical coverage, assuming one MPTMS molecule to react with one SiOH molecule. The actual coverage is calculated from the C contents, also assuming one methoxy group reacted. The grafting yield is the ratio between this actual coverage and the theoretical coverage. Its accuracy depends both on the accuracy of the C content measurements and the effective grafting reaction. The error is the largest for the smallest ratio MPTMS/SiOH

CP/MAS spectra of the surface of the silica before and after modification. Typical spectra are shown in *Figure 1*. Most of the surface silicon atoms of the initial silica (*Figure 1a*) carry only one Si–OH group and just a few have two OH groups on the same silicon atom. However, the grafting reaction may involve two (or even three) neighbouring Si–OH groups of the surface. After grafting (*Figure 1b*), there is evidence for MPTMS molecules grafted by only one or two siloxane bonds, as shown by the two new peaks (D, E) appearing at −49 and −58 ppm. However, there are probably not too many molecules grafted by three siloxane bonds, which should be indicated by a peak at −66 ppm. The attribution of these peaks is reported in *Table 2* from the data published recently by de Haan *et al.*[30].

The second reason for the limitation of the grafted groups might be the limit of monolayer coverage by MPTMS molecules. It would mean that each MPTMS molecule can cover 71 Å^2, which is close to the value that can be estimated from its structure. The monolayer hypothesis seems to be well accepted now[31]. The recent study of Vrancken *et al.*[32] concluded that a similar molecule, aminopropyltriethoxysilane, covers 64 Å^2 of the surface of dried silica.

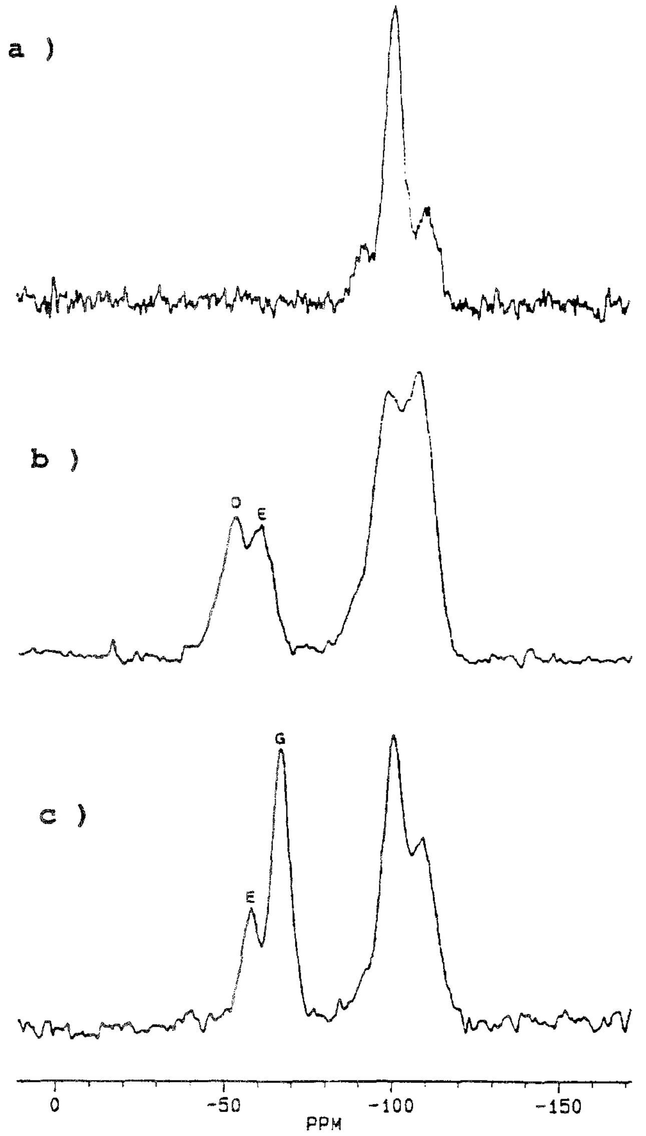

Figure 1 ^{29}Si n.m.r. CP/MAS spectra of: (a) dried silica; (b) silica after grafting of MPTMS in toluene; (c) grafted silica redispersed in water

It follows that, if one wants to graft more coupling agent, it is necessary first to cause some polycondensation of the coupling agent in order to attach a set of molecules on the same point at the surface. Actually, a few experiments have shown that, if no special precaution is taken to dry both the silica and the reactants, more MPTMS can be grafted. However, it is difficult to control this amount by just adding given amounts of water. It is safer to react the coupling agent previously with water in solution. In such a reaction, first, hydrolysis of the alkoxy groups occurs rather rapidly, while the condensation reaction is much slower. These reactions can be followed by ^{1}H n.m.r.: upon hydrolysis, the resonance of the methoxy groups at 3.52 ppm from tetramethylsilane (TMS) disappears. The data shown in *Figure 2* are in good agreement with the results published recently by Babonneau *et al.*[33], so that it can be estimated that enough condensation has been obtained after 2 h at pH 2 in methanol. When the product is reacted with silica, the grafting yield is increased up to 62%, instead of the 33% in a typical run.

The samples used later in this study have been obtained in this way and their carbon contents are thus higher than 7%. The reason is that complete dispersion of functionalized silica in toluene, as judged by the size average of the particles, involves a high degree of functionalization; surprisingly, for a coverage corresponding to a monolayer,

Table 2 ^{29}Si CP/MAS assignments after ref. 30[a]

Structure	X	Y	Shift (ppm from TMS)
Si–O–Si(R)XY	OH	OH	−49
	OR′	OH	−49
	OR′	OR	−49
$(SiO)_2SiRX$	OH		−58
	OR′		−58
$(SiO)_3$–SiR			−66
$(SiO)_4$–Si			−111
$(SiO)_3$–SiOH			−101
$(SiO)_2$–$Si(OH)_2$			−91.7

[a] TMS=tetramethylsilane; R,R′ = alkyl groups

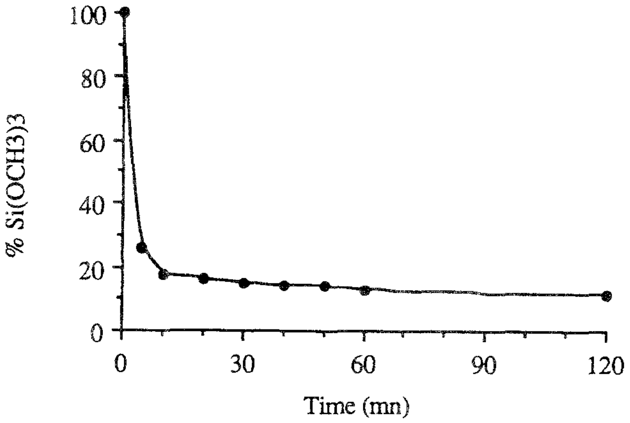

Figure 2 Percentage of methoxy groups of MPTMS remaining after hydrolysis at pH 2 (MPTMS/H_2O/CH_3OH molar ratio 1/3/2) *versus* time (min)

a broad distribution of particle size (between 10 and 50 nm in diameter) is observed by q.e.l.s. If the coverage is far from complete (0.87 μmol m^{-2}), large agglomerates (300 nm) are observed. It is only when partly condensed MPTMS is used that the initial size of the silica (13 nm) is observed again.

Dispersion in water

Before being engaged in emulsion polymerization, the functionalized silica, which is strongly hydrophobic, must be redispersed in water. It is first separated from toluene, washed with methanol and dried, to give a powder that is finely ground.

Even in the presence of surfactants such as sodium dodecyl sulfate or sodium ethylhexyl sulfosuccinate, the finely ground powder gives agglomerates in water. It gets dispersed very slowly when the pH is increased to 9.5. However, after 3 days a broad distribution of small agglomerates is observed, as shown in *Figure 3a*. A much better dispersion is obtained if a wetting agent (isobutanol) is added and the suspension is sonicated for a few hours (*Figure 3b*).

Such treatment causes the silica to become more hydrophilic; this change corresponds to some chemical modification of the surface, as can be demonstrated by n.m.r. CP/MAS analysis. As shown in *Figures 1b* and *1c*, the peak at −49 ppm from TMS disappears while a new peak at −66 ppm appears. The assignments of these peaks according to de Haan *et al.*[30] are reported in *Table 2*. The modifications observed involve two kinds of reactions: hydrolysis of the alkoxy groups, and condensation of silanol groups in siloxane bridges. The relative increase of the peak at −101 ppm *versus* the peak at −111 ppm might be due to hydrolysis of the Si–O–Si bond linking the MPTMS to the surface of the silica. However, as shown by elemental analysis and also by ^{13}C n.m.r. CP/MAS (*Figure 4b*), most of the coupling agent remains fixed to the silica. The hydrolysis of the alkoxy group is confirmed by the ^{13}C n.m.r. analysis, as shown in *Figure 4*; the major change is the elimination of the peak at 53 ppm. All the other peaks, which correspond to the various carbon atoms of the methacryloxylpropyl group, are still present after the treatment, although some minor modifications can be observed. This statement is confirmed by the elemental analysis; the carbon content is slightly decreased from 7.8% to 7.0%, while the silicon content increases from 47.6% to 48.8%. The decrease of the carbon content corresponds rather well to the hydrolysis of one methoxy group for one methacryloyl moiety remaining on the surface of the silica.

A number of trials have been done with the aim of improving the dispersion state of the silica; unfortunately they were unsuccessful. The different ways tried were the following:

(i) From silica with less MPTMS grafted. Such silica, with MPTMS carbon content of 2 or 2.9% instead of 7%, is much more hydrophilic and, at pH 9.5, even in the absence of isobutanol, is easily dispersed in water. However, the dispersed particles are actually aggregates, which do not disappear even after several days under stirring, and even if isobutanol is added. The smallest size obtained is 120 nm for carbon content of 2.9% and 180 nm for 2%. It seems that, when the

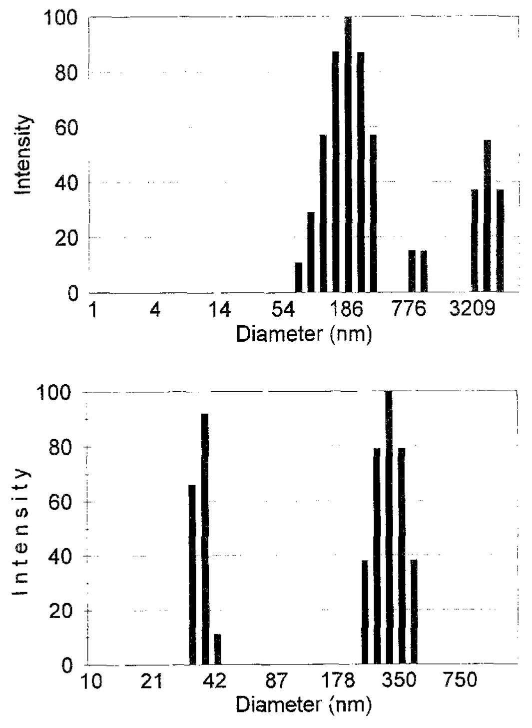

Figure 3 Quasi-elastic light scattering data showing the size distribution of particles (or agglomerates) of functionalized silica dispersed and stirred in water at pH 9.5 for 3 days, (a) in the absence or (b) in the presence of 0.4% isobutanol

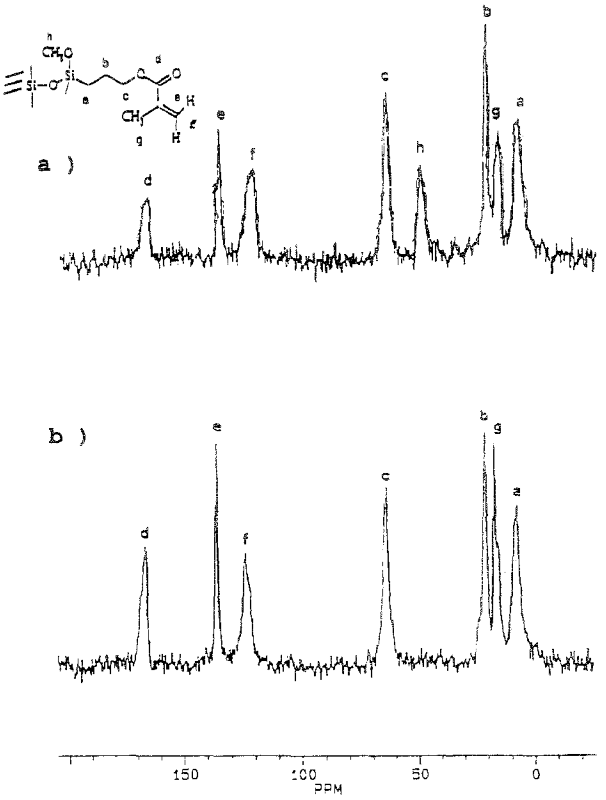

Figure 4 ^{13}C n.m.r. CP/MAS spectra of MPTMS grafted silica: (a) after functionalization in toluene; (b) after dispersion in water (+ 0.4% isobutanol) at pH 9.5

Table 3 Dispersion of silica in mixtures of toluene and isobutanol

Isobutanol (vol%)	Particle diameters (nm) from q.e.l.s.
20	12, 160, 1000, 4000
40	12, 120, 600
60	12, 100, 400

grafting was not high enough to destroy the aggregates in toluene, these initial aggregates remain. When they are introduced into water, they tend to aggregate again due to hydrophobic interactions. These interactions are only partly compensated by the use of dispersing agents (isobutanol, surfactants) or by chemical modification after treatment at high pH.

(ii) A second approach was to use mixtures of isobutanol and toluene to carry out the functionalization. Before functionalization, the dispersions of diluted suspension (1% weight) of silica in mixtures containing between 10 and 60% of isobutanol in toluene have been studied. Light scattering studies of the particle sizes can be carried out if the isobutanol content is higher than 20%; then various families of particles can be observed, as reported in *Table 3*. Individual particles (12 nm) can be observed as the major family, corresponding to the actual size of the silica, as given by the manufacturer. Then, functionalization has been carried out by reacting the MPTMS with the silica dispersed (1% weight) in toluene containing 20% isobutanol. The carbon content was 2.9%, and the size analysis after grafting again shows four families of particles with diameters of 14, 90, 800 and 2000 nm. However, when the silica, after separation, through a few cycles of washing and centrifugation, is dispersed in water at pH 9.5, aggregation takes place again and the smaller diameter is 120 nm.

CONCLUSION

Starting from dry silica, functionalization by reacting a functionalized trialkoxysilane coupling agent can be easily carried out in toluene to give a monolayer. Partial condensation of the coupling agent prior to grafting is the best way to graft more than the monolayer. The more difficult process is then the redispersion in water of the functionalized silica, owing to its highly hydrophobic character. Hydrolysis of the non-reacted alkoxy groups at high pH, and the use of isobutanol as a dispersing agent, give the best dispersion state, characterized by a rather monodisperse family of small aggregates of a few initial silica particles.

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