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Synthesis of composite latex particles filled with silica

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SUMMARY: Encapsulation of silica nanoparticles was performed by dispersion polymerization of styrene, butyl acrylate and butyl methacrylate in aqueous alcoholic media. Following previous works[1-3], the silica beads were first modified by reacting on their surface the 3-trimethoxysilyl propyl methacrylate coupling agent (MPS). In every case, the silica beads are all surrounded by polymer giving composite latex particles filled with silica. Each composite particle contains from one to a great number of silica beads. Changing the size or the concentration of the silica beads, and the experimental conditions for the synthesis of the polymer particles enables to control this number. One can take benefit of this to synthesize model composite particles with controlled compositions.

Introduction

Highly dispersed modified or unmodified oxide nanoparticles are widely used as pigments, fillers or additives in polymer industry. The surface properties and the particle size distribution of these oxides are important characteristics determining the degree of interaction of the filler with the polymer matrix. Indeed, due to their hydrophilicity, the oxide surfaces, as for instance silica surfaces, are very difficult to wet with polymers in particular if the later does not contain groups capable of interacting with the oxide. Therefore, modifications of the filler surface using for example coupling agent or proadhesives compounds as surfactant or dispersants, are frequently used to modify the inorganic/organic interphase resulting in increased dispersability and stability of the system. In recent years, it appeared of great interest to realize this compatibilization in situ by polymerizing directly at the surface of the filler and covering the oxide with a polymer layer[4, 5]. Hybrid polymer-inorganic nanocomposites have retained particular attention in several domains with applications as optical, magnetic or reinforcing agent materials[6]. Polymer-protected metal nanoparticles also offer a lot of interesting features in catalysis[7]. Our goal in the present study is to encapsulate silica nanoparticles and to control the morphology of the composite particles by dispersion polymerization. As a matter of fact, it is expected that the distribution of the silica beads into the polymer particles will control the final arrangement of the filler in the polymer matrix. In addition to the potentialities of these

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encapsulated fillers in many industrial applications, such composite particles may also be interesting models for a more comprehensive study of the mechanical behaviour of filled polymers.

Experimental details

Materials

The reagents for the synthesis and modification of the silica beads, tetraethylorthosilicate, ammonia, 3-trimethoxysilyl propyl methacrylate (MPS), absolute ethanol, the initiator, 2.2'-azobis (isobutyronitrile) (AIBN) and the stabilizers, poly (N-vinyl pyrrolidone) (PVP K30, M_w=40000 g/mole and PVP K90, M_w=360000 g/mole), poly(styrene-b-ethylene oxide) (SE3030, M_w=6000 g/mole), have the same origin as in the previous works[1-3)]. The macromonomer, polyethylene oxide terminated monomethacrylate (MA-PEO, M_w=2000 g/mole) was supplied by ICI paints and used without further purification. The monomers, styrene, butyl acrylate and butyl methacrylate from Aldrich were purified by distillation before use.

Synthesis and modification of the silica beads

Colloidal silica sols (alcosols) with particles size varying from 29 nm to 629 nm have been synthesized according to the procedure of Stöber et al.[8)] in a mixture of ethanol and water from tetraethylorthosilicate and ammonia. Grafting of the silica beads was done by adding directly in the same medium an excess of the MPS coupling agent. The alcosol was purified from unreacted coupling agent by dialysis as described previously[1].

Polymerization reactions

The dispersion polymerisation was performed in batch at 60°C or 70°C, by mixing the stabilizer, the initiator and the monomer in an ethanol water medium with the desired composition, and containing various concentrations of the grafted silica beads (from 0 to 1.5g per 100g of total solvent). The concentrations (in g per 100g of solvent) of all the others components are: monomer: 10wt%, AIBN: 0.1wt% and various concentrations of the stabilizers: from 0.5 to 2wt%.

Characterization

The molecular weights and molecular weight distributions were measured by gel permeation chromatography[3]. Particle sizes were measured using a Coulter laser diffraction granulometer (LS 230). The polymer conversions were determined gravimetrically. The number of polymer particles was deduced from the particle size and polymer conversion. The silica-polystyrene composite particles were analysed by transmission electron microscopy (TEM) using Philips CM10 and CM200 microscopes. The average number of silica beads per particle (N_a), which corresponds to the ratio of the number of silica beads over the total number of latex particles, was determined from the TEM micrographs as described elsewhere[1-3]. Due to the very low glass transition temperature (Tg) of polybutylacrylate (PBA, Tg=-55°C), cryo-TEM was performed to observe in this case the composite particles in a preserving thin film of vitreous ethanol/water diluent. If the thickness of the embedding film is larger than the diameter of the particles, the measurement of diameters is reliable. When this was not the case, we used the average diameters obtained by the Coulter analysis to calculate N_a.

Control of polymer particle size in dispersion polymerization

In that part of the study, our goal was to find experimental conditions leading to polymer particles having very different diameters. Indeed, we will next demonstrate that the size of the polymer particles synthesized in the absence of silica beads in the medium, is a determining parameter, which controls the composition of the composite particles. For that purpose, blank experiments, i.e., polymerization reactions without silica beads, were performed by changing for instance the nature or concentration of the stabilizer and the nature of monomer or solvent composition. As a matter of fact, all these parameters are known to influence significantly the particle sizes and also the molecular weight of the polymers synthesized in dispersion polymerization. Three different polymers have been investigated having different glass transition temperatures. PBA and polybutylmethacrylate (PBMA) with low Tg (–55°C and 32°C, respectively) are compared to the more glassy polystyrene (PS, Tg=100°C). We expect that changes in the Tg and in the nature of the polymer will also induce changes in the morphology of the composite particles. In addition, by decreasing the Tg of the polymer, one facilitates the film formation at room temperature, which is essential for the study of the mechanical properties of the composites. The results, including conversion, particle size, particle number and molecular weight, are given in the following Tables 1 to 3 for PS, PBMA and PBA, respectively.

Tables 1-3: Polymer conversion, particle diameter, particle number, molecular weight and molecular weight distribution as a function of the nature or concentration of the stabilizer and of the solvent composition for the three polymers synthesized in the absence of silica [a].

Table 1. Polystyrene (PS) synthesis

Entry	Stabilizer		Solvent composition	Polymer	Particle diameter[d]	Particle number	Molecular weight (g/mole)	
n°	Type	Wt% [b]	$\mathrm{EtOH/H_2O}$	g/l [c]	D_p (nm)	N_p / l [c]	M_n	M_w/M_n
1	PVP K30	2	94.5/5.5	68	750	3.1 10^{14}	29000	3.8
2	PVP K30	2	70/30	85	312	5.3 10^{15}	91870	9.5
3	PS/PEO	0.5	94.5/5.5	68	141	4.6 10^{16}	73650	4.2
4	PS/PEO	1	94.5/5.5	74	75	3.3 10^{17}	81260	3
5	PS/PEO	2	94.5/5.5	78	62	6.2 10^{17}	98450	1.9

Table 2. Polybutylmethacrylate (PBMA) synthesis

Entry	Stabilizer		Solvent composition	Polymer	Particle diameter[e]	Particle number	Molecular weight (g/mole)	
n°	Type	wt% [b]	$\mathrm{EtOH/H_2O}$	g/l [c]	D_p (nm)	N_p / l [c]	M_n	M_w/M_n
6	PVP K90	2	70/30	85	1145	1.1 10^{14}		
7	PVP K90	2	50/50	89	709	4.8 10^{14}	59734	2.3
8	MA-PEO	2	70/30	85	480	1.5 10^{15}	33552	2.4

Table 3. Polybutylacrylate (PBA) synthesis

Entry	Stabilizer		Solvent composition	Polymer	Particle diameter[e]	Particle number	Molecular weight (g/mole)	
n°	Type	wt% [b]	$\mathrm{EtOH/H_2O}$	g/l [c]	D_p (nm)	N_p / l [c]	M_n	M_w/M_n
9	PVP K90	2	70/30	85	1124	1.1 10^{14}	6402	4.2
10	PS/PEO	2	70/30	85	657	5.7 10^{14}	5800	4.4
11	MA-POE	0.5	70/30	84	86	2.5 10^{17}	10185	3
12	MA-PEO	1	70/30	85	60	7.5 10^{17}	6193	5
13	MA-PEO	2	70/30	76	57	7.8 10^{17}	8367	3.15

[a] The polymerization reactions were performed under the following conditions: total solvent, 100g; AIBN, 0.1g; monomer, 10g. [b] In grams per 100 g of solvent. [c] Per liter of solvent.
[d] TEM analysis. [e] Coulter analysis. Temperature: 60°C for PS and 70°C for PBA and PBMA.

The results in Table 1-3 indicate that for each of the three polymers, it is possible to find experimental conditions giving small, medium or large polymer particles. The largest particle sizes, with diameters comprised between 750 and 1200 nm (entries 1, 6 and 9), are obtained using the poly N-vinyl pyrrolidone homopolymers PVP K30 or PVP K90. In the case of PS and PBMA, it is possible to lower this size by increasing the amount of water in the polymerization medium (entries 2 and 7). Medium particle sizes are obtained for PBA using the poly(styrene-b-ethylene oxide) block copolymer (see entry 10), meanwhile the same stabilizer gives small polymer particles in the case of PS (entries 3, 4 and 5). Polymer particles with very low sizes are also obtained in the case of PBA using the MA-PEO macromonomer as stabilizer (entries 11, 12 and 13), but attempts to synthesize such small polymer particles did not succeed in the case of PBMA (entry 8). Concurrently, Table 1 shows that a decrease in the particle size is accompanied by an increase of the molecular weight of the polymer, in agreement with the mechanism of dispersion polymerization. The very low molecular weight values given in Table 3 in the case of PBA, are probably due to transfer reactions, which are known to take place on this polymer. So, the above results demonstrate that it is possible, for the three polymers of the series, to change significantly the size and therefore the number of polymer particles in the blank experiments by simply changing the experimental conditions. Variations of almost four orders of magnitudes are observed between the lowest and the highest values of the polymer particle number (N_p/l is varying from 10^{14} to around 10^{18}).

Synthesis of the composite latex particles

In the following, composite latex particles are synthesized in presence of MPS grafted silica beads having different sizes and concentrations. We prove by TEM, that whatever the size or concentration of the silica beads, or the nature of the monomer and/or stabilizer, all the silica beads are surrounded by polymer and are therefore encapsulated. Figure 1 shows for example several small silica beads embedded into large PS particles. In that case, the number, N_a, of silica beads per particle can be expressed as a function of the average diameters of the silica beads and composite particles3). Low N_a values indicate the formation of latex particles without silica beads, while high N_a corresponds to composite particles containing several silica beads. Our goal is to demonstrate how it is possible to control and thus to predict the value of N_a by simply changing the experimental conditions for the synthesis of the composite particles.

It may be effectively interesting to obtain whatever the size of the silica beads between 29 nm and 629 nm, composite particles containing only one silica bead. Such a control appears possible if one considers that the overall number of particles (composite and free latex particles) obtained in presence of the silica beads is similar to that obtained in the blank experiments. Consequently, N_a can be predicted from the ratio of the number of silica beads introduced in the polymerization reaction over the number of polymer particles obtained in the blank. We have plotted in Figure 2 the evolution of the number of silica beads as a function of their size ranging from 25 nm to 650 nm for a low and a high bead concentration.

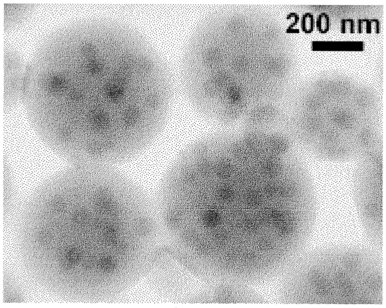

Fig. 1: TEM micrograph of small silica beads encapsulated with polystyrene.

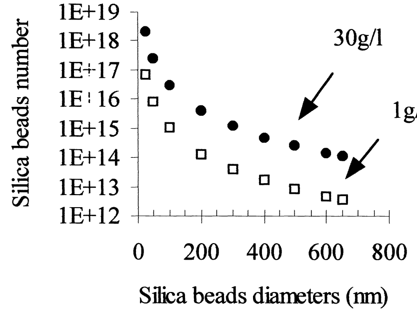

Fig. 2: Evolution of the number of silica beads per liter as a function of the silica beads size.

It clearly appears that the overall number of silica beads changes considerably, from around 10^{13} to 10^{18} when decreasing the size from 650 to 25 nm. Notice that the silica beads concentration in the range 1 to 30 g/l has only a small effect on the particle number. In addition, we have shown previously that the number of polymer particles in the blank experiments can be varied from 10^{14} to around 10^{18} by an appropriate choice of the experimental conditions. Therefore, it must be possible to obtain very different values of Na by an appropriate choice of the number of silica beads and of the experimental conditions for the synthesis of the latex particles. For instance, if the number of silica beads introduced in the encapsulation reaction is larger than the number of polymer particles obtained in the blank experiments, we can anticipate that each composite particle will contain several silica beads. This is illustrated in Figure 1 for PS and in Figure 3a for PBMA which both correspond to experiments performed with PVP as stabilizer and small silica beads (72 nm in diameter, see Tables 4 and 5 below). If the number of silica beads is more or less equal to the number of polymer particles synthesized in the blank experiment, it can be predicted that N_a will be close to one. This is indeed verified in Tables 4 and 5 for different sizes of the silica beads and the different monomers. An illustration is given in Figure 3b for PBA. Finally, if the number of silica beads is lower than the number of polymer particles synthesized in the absence of silica, we can expect that some polymer particles without silica beads will also be formed in addition to the composite particles, which means that N_a will be lower than one. This is confirmed again by the results of Tables 4 and 5 and illustrated in Figure 3c in the case of PBA. So, all these examples and others obtained as a part of this work, have proved that the composition of the composite particles can be efficiently controlled by an appropriate choice on the one hand, of the size and concentration of the silica beads, and on the other hand, of the experimental conditions for the dispersion polymerization, i.e., the nature and concentration of the monomer or stabilizer, the solvent composition, etc...

Table 4. Silica-polystyrene (SiO_2-PS) composite particles [a]

	Stabilizer	PVP K30			PS/PEO		
Silica beads	Diam. (nm) [b]	13	72	352	29	108	300
Silica beads	$N_p(SiO_2)$ [c]	$5.8\ 10^{18}$	$3.4\ 10^{16}$	3.10^{14}	$5.2\ 10^{17}$	10^{16}	$4.7\ 10^{14}$
Blank Polym.	Part. nbr [c]	$3.1\ 10^{14}$	$3.1\ 10^{14}$	$3.1\ 10^{14}$	$6.2\ 10^{17}$	$6.2\ 10^{17}$	$6.2\ 10^{17}$
Composites	N_a [d]	3158	23	1.3	0.97	0.026	0.0008

[a] Polymerization conditions: 60°C, EtOH, 94.5g; water, 4.5g; total solvent, 100g; AIBN, 0.1g; styrene, 10g; stabilizer, 2g; SiO_2, 1.5g. [b] Determined by TEM. [c] Number of particles per liter of solvent. [d] Determined from TEM analysis of the composite particles.

Table 5. Silica-polybutylmethacrylate (SiO_2-PBMA) and silica-polybutylacrylate (SiO_2-PBA) composite particles

		SiO_2-PBMA [a]		SiO_2-PBA [a]			
	Stabilizer	PVP K90	PVP K90	PVP K90	PS/PEO	MA-PEO	MA-POE
Silica beads	Diam. (nm) [b]	72	264	62	264	32	73
Silica beads	Conc. (wt%)[c]	1	0.25	1	1.1	1.6	1
Silica beads	$N_p(SiO_2)$ [d]	$2.3\ 10^{16}$	$1.2\ 10^{14}$	$3.8\ 10^{16}$	$5.4\ 10^{14}$	$4.4\ 10^{17}$	$2.3\ 10^{16}$
Blank Polym.	Part. nbr [d]	$1.1\ 10^{14}$	$1.1\ 10^{14}$	$1.1\ 10^{14}$	$5.7\ 10^{14}$	$7.5\ 10^{17}$	$7.5\ 10^{17}$
Composites	N_a [e]	99	1.9	250	1.6	0.6	0.05

[a] Polymerization conditions: 70°C, EtOH, 70g; water, 30g; total solvent, 100g; AIBN, 0.1g; monomer, 10g; stabilizer, 2g except for MA-PEO, 1g. [b] Determined by TEM. [c] In g per 100g of solvent. [d] Number of particles per liter of solvent. [e] Determined from the Coulter analysis of the composite particles.

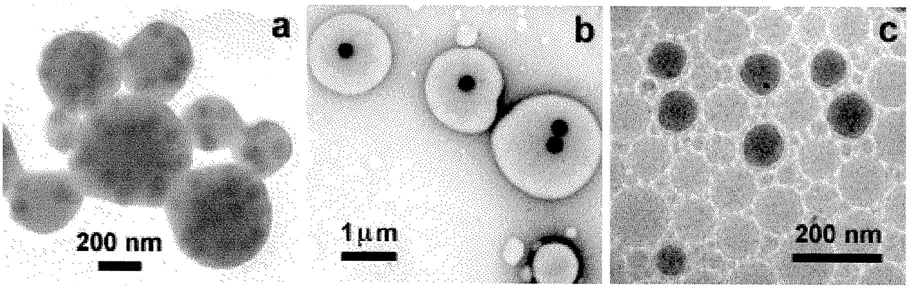

Fig. 3: TEM micrographs of composite particles with PBMA (a) and PBA (b, c): (a) $N_a>1$ (dry without stain); (b) $N_a \sim 1$ (dry with negative stain. The polymer flattened around the embedded particle); (c) $N_a<1$ (image recorded at low temperature in a thin film of vitreous EtOH/H_2O). Silica beads are in dark.

Conclusion

Encapsulation of small MPS grafted silica beads was performed by dispersion polymerization of styrene, butyl acrylate and butyl methacrylate in a mixture of ethanol and water. We demonstrate that it is possible to predict the number of silica beads per composite particles by controlling the experimental conditions for the synthesis of the composite particles. We are able to obtain composite particles containing less than one, close to one and more than one silica beads, whatever the size and concentration of the silica beads and the nature of the monomer.

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