

# Nanocomposite particles with core–shell morphology III: preparation and characterization of nano $\text{Al}_2\text{O}_3$ – poly(styrene–methyl methacrylate) particles via mini-emulsion polymerization

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**Abstract** Encapsulation of inorganic nanoparticles (as a core) by polymers (as a shell) is one of the interesting research subjects that lead to the synthesis of nanocomposite. These materials include properties of not only the organic polymer (e.g. optical properties, toughness, processability, flexibility, etc.) but also the inorganic nanoparticles (e.g. mechanical strength, thermal stability, etc.). Some of the applied preparative methods are dry-spray, dispersion, suspension, emulsion and mini-emulsion polymerization techniques. Here, mini-emulsion polymerization technique was used in order to obtain white-color nanocomposite latex particles containing nano-alumina (40–47 nm) encapsulated by copoly [styrene (St)–methyl methacrylate (MMA)] under high-shear ultrasonic irradiation. At first, bare nano-alumina was encapsulated with the copolymer to obtain latex particles. In another attempt and in order to investigate the effect of compatibilizing system, alumina nanoparticles were coated with oleic acid in order to form modified alumina core. Then mini-emulsion polymerization was performed in the mini-droplets including modified alumina, St and MMA for obtaining core/shell nanocomposite particles. The progress of encapsulation polymerization was followed by different instrumental techniques such as FT-IR spectra, thermal gravimetric analysis, dynamic light scattering, induced-coupled plasma, TEM and SEM.

**Keywords** Mini-emulsion polymerization · Nano-alumina · Nanocomposite particle · Encapsulation · Ultrasound

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## Introduction

Several patents [1, 2] and papers [3] deal with the encapsulation of colloidal metals, sol–gel type inorganic oxides particles ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ) [4] and other inorganic pigments to give organic–inorganic hybrid dispersions, where the polymer shell is built in situ by means of conventional emulsion [5–8], miniemulsion [9–15] and related dispersed-phase polymerization processes.

Encapsulation of inorganic nanoparticles as a core by polymers as a shell forms core/shell structures containing not only polymer properties but also inorganic nanoparticle properties. Extensive research has been reported involving various inorganic particles, such as, calcium carbonate, silica, titanium dioxide [16–21], carbon black [22] and magnetite [4, 23] with either micrometer or nanometer sizes.

Alumina nanoparticles are of much interest because of their high hardness, high strength, and good wear resistance [24]. They have widely been used as fillers for polymers for improvement of the mechanical, tribological, barrier, and conductive properties [25–27].

Duguet et al. [28] have reported encapsulation of spherical submicron size alumina particles through suspension polymerization. Guo and coworkers [29] have also reported encapsulation of needle-shaped nanosize alumina with polystyrene (PS) through emulsion polymerization. It seems that spheres are easier to be encapsulated than needles due to easier stabilization by the reaction medium.

*Conventional* miniemulsions are aqueous dispersions of relatively stable dispersed minidroplets with a size less than 500 nm. They are prepared at high shears in a system containing oil, water, a surfactant and a highly water-insoluble compound (hydrophobe) to suppress Ostwald ripening of the droplets [30]. The polymerization of such miniemulsions extends the possibilities of widely applied emulsion polymerization and provides advantages with respect to incorporation of hydrophobic compounds and composition of the oil phase [31].

On the other hand, ultrasonic cavitations can generate local high temperature and high pressure and a very rigorous environment for chemical reaction [32]. Under these rigorous conditions, radicals can be generated due to the decomposition of water, monomer, surfactant, or rupture of polymer chains to initiate the polymerization of monomer [33].

Duguet et al. [28] applied 3-methacryloxy propyl trimethoxy silane (MPTMS) as a reactive coupling agent to chemical modification of alumina particles surface. Ding et al. [34] used oleic acid as a functionalized monomer because the C=C bonds of oleic acid can be copolymerized with styrene (St) monomer. They reported that oleic acid could bond to the silica surface through hydrogen bonding. Surface-modified silica nanoparticles were then used in the encapsulation polymerization process. St monomer added to fully dispersed silica particles modified by oleic acid as seeds, was copolymerized with the oleic acid via in situ emulsion polymerization, in the presence of an initiator. We have also used silica-modified nanoparticles with oleic acid through miniemulsion polymerization reaction for obtaining nanocomposite particles with core/shell morphology and the role of oleic acid as a compatibilizing agent was investigated too [16].

In this study, encapsulation of alumina nanoparticles with copoly [St–methyl methacrylate (MMA)] was performed for preparation of spherical nanosize alumina/copoly (St–MMA) nanocomposite particles by miniemulsion polymerization under ultrasonic irradiation. Also, alumina nanoparticles were coated with oleic acid to obtain modified alumina and then they were incorporated into the miniemulsion polymerization in order to obtain core/shell particles with copoly (St–MMA) as the shell and nano-alumina or modified nano-alumina as the core.

## Experimental

### Materials

Styrene with 20 ppm inhibitor from Merck Chemical Co. (analytical grade) was washed with 5 wt% aqueous sodium hydroxide to remove the inhibitor, dried over calcium chloride and stored at 0 °C. MMA, oleic acid, span80, hexadecane (HD) and benzoyl peroxide (BPO) from Merck Chemical Co., sodium dodecyl sulfate (SDS) and nano- $\text{Al}_2\text{O}_3$  particles with size of 40–47 nm from Aldrich were used without further purification.

### Apparatus

Fourier transform infrared (FT-IR) spectra of the samples in KBr pellets were recorded on a FT-IR BRUKER-IFS 48 spectrophotometer (Germany). Thermal gravimetric analyses (TGA) were recorded on a STA-PL instrument (England). The essential operations were carried out according to the manufacture's instructions. The samples were weighed on a Shimadzu LIBRORE AEU-210 analytical electrobalance to a precision of 0.0001 g for this analysis. SEMATECH light scattering (France) with 633 nm wavelength was used to obtain size of the nanoparticles through dynamic laser light scattering (DLS). The morphology of alumina nanoparticles and formation of the copoly (St/MMA) shell layer around the nano-alumina particles were investigated by transmission electron microscopy (TEM) on a ZEISS 902A (Germany). The samples were diluted up to 20 times and dropped on a copper grid and dried. The morphology of samples was also characterized by scanning electron microscopy (SEM) on a XL30 instrument from Philips Company (Netherland). The equipment employed to generate ultrasonic irradiation was a SONOPLUS Ultrasonic homogenizer, HF-GM 2200 from BANDELIN electronic GmbH & Co, KG (Germany) with a frequency of  $20 \pm 0.5$  kHz and a titanium probe MS-73 with diameter of 3 mm. In some steps, material dispersions were prepared in a Julabo Labortechnik GMBH D-733 Seelbatch (Germany) ultrasound bath with frequency of 35 kHz. Induced coupled plasma-optical emission spectroscopy (ICP-OES) analyses were recorded on an ICP-OES CCD, Vista-Pro model, from Varian Company (Italy).

### Pretreatment of nano-alumina with oleic acid (m-Al<sub>2</sub>O<sub>3</sub>)

Alumina (1 g), oleic acid (1 ml) and 50 ml distilled water were added into the sonochemical reaction vessel. Ultrasonic irradiation was carried out with the probe of ultrasonic horn immersed directly into the mixture for 5 min. The aqueous ammonia (5 ml, 25 wt%) was added to the above mixture, irradiated with ultrasonic for 5 min and stirred with magnetic stirrer for 2 h. The mixture was demulsified by adding HCl (20 wt%) dropwise. The liquid phase was decanted. Redispersion of the white residue in methanol (95%) was achieved by ultrasonic bath. After 5 min, modified nano-alumina was precipitated, separated and dried at 50 °C for 10 h. The amount of adsorbed oleic acid onto the surface of alumina nanoparticles was 7.5 wt% relative to the total amount of obtained product.

### Miniemulsion polymerization

#### *Typical procedure for encapsulation of nano-alumina*

The process to obtain nanocomposite latexes was as follows: typically, the mixture of nano-alumina (0.69 g), St (7.7 ml) and MMA (7.2 ml) (molar ratio of 1:1 for monomers) with 2.2 ml HD and 0.5 ml span 80 were added into the sonochemical reaction vessel and mixed by ultrasonic irradiation for 5 min just before use. Then a solution of 0.29 g SDS in definite amount of distilled water (62 ml) was introduced and sonicated for 10 min. After miniemulsion was formed, the above mixture with 0.27 g BPO (initiator) was moved into a 500 ml round bottomed reactor equipped with a mechanical stirrer and condenser, under nitrogen atmosphere to prevent probable inhibition. The reaction temperature was set at 70 °C and stirring rate was fixed at 300 rpm in the whole process. Sampling was carried out every 1 h along the progress of reaction (it was completed after 10 h) and each sample was inhibited with 1 ml solution of hydroquinone/methanol (1% W/V). Samples were dried at room temperature and used to obtain the conversion amount.

#### *Typical procedure for encapsulation of modified nano-alumina*

The mentioned procedure in above section (3-4-1) was also applied for preparation of latexes containing modified nano-alumina (m-nano Al<sub>2</sub>O<sub>3</sub>).

The detailed recipe (Tables 1, 2) summarizes two series of encapsulation experiments.

## Results and discussion

In order to obtain successful encapsulation process, it was necessary to achieve good particles dispersion in the monomers phase and obtaining stable minidroplets of monomers containing inorganic nanoparticles. The stabilization system contained Span80 and SDS as surfactants and HD as hydrophobic agent. In other attempt and in order to investigate the effect of modifiers of nanoparticles, nano-alumina

**Table 1** Typical recipe used for the encapsulation of alumina nanoparticles

Components	SMA-1	m-SMA-1
Styrene	7.7 ml (0.067 mol)	7.7 ml (0.067 mol)
Methyl methacrylate	7.2 ml (0.067 mol)	7.2 ml (0.067 mol)
nano- $\text{Al}_2\text{O}_3$	5 wt% <sup>a</sup>	–
m-nano $\text{Al}_2\text{O}_3$	–	5 wt% <sup>a</sup>
SDS	2wt% <sup>b</sup>	2 wt% <sup>b</sup>
HD	12 wt% <sup>b</sup>	12 wt% <sup>b</sup>
Span 80	3.5 wt% <sup>b</sup>	3.5 wt% <sup>b</sup>
BPO	2 wt% <sup>a</sup>	2 wt% <sup>a</sup>
Distilled water	80 wt% <sup>b</sup>	80 wt% <sup>b</sup>

<sup>a</sup> Weight percent relative to the total amount of monomers

<sup>b</sup> Weight percent relative to the total amount of monomers and nano- $\text{Al}_2\text{O}_3$  or m-nano  $\text{Al}_2\text{O}_3$

**Table 2** Recipes used for preparation of different samples

Sample	St	MMA	nano- $\text{Al}_2\text{O}_3$	m-nano $\text{Al}_2\text{O}_3$	SDS	HD	Span 80	BPO	Water	Coagulation <sup>a</sup> (%)
Blank	7	6.7	0	0	0.3	1.7	0.9	0.3	59	0
SMA-1	7	6.7	0.7	–	0.3	1.7	0.5	0.3	62	0.9
SMA-2	7	6.7	1.4	–	0.3	1.8	0.5	0.3	65	2.7
SMA-3	7	6.7	2.1	–	0.3	1.9	0.6	0.3	68	16.9
SMA-4	7	6.7	2.8	–	0.3	2.0	0.6	0.3	71	20.4
m-SMA-1	7	6.7	–	0.7	0.3	1.7	0.5	0.3	62	0.1
m-SMA-2	7	6.7	–	1.4	0.3	1.8	0.5	0.3	65	1.0
m-SMA-3	7	6.7	–	2.1	0.3	2.0	0.6	0.3	68	0.8
m-SMA-4	7	6.7	–	2.8	0.3	2.0	0.6	0.3	71	6.1

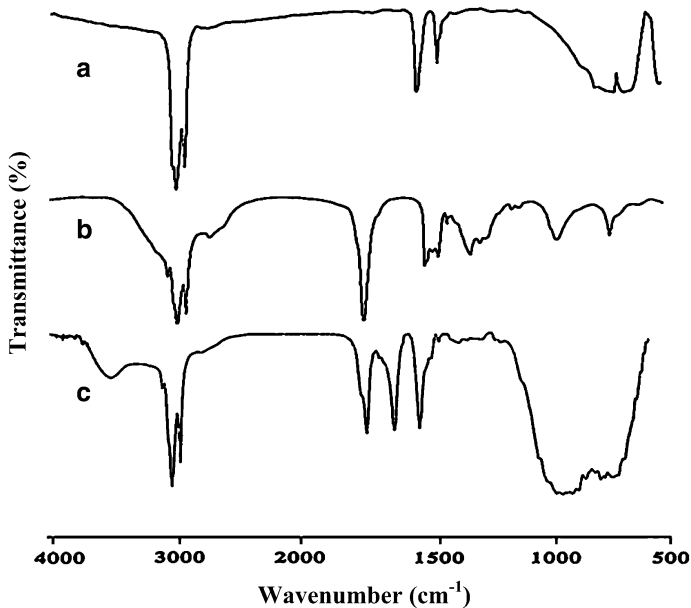
All reported amounts are in gram

<sup>a</sup> Weight percent relative to the total amount of monomers and nano- $\text{Al}_2\text{O}_3$  or m-nano  $\text{Al}_2\text{O}_3$

particles were coated with oleic acid to change their hydrophilic characteristic into the hydrophobic ones. With the aid of ultrasonic irradiation, minidroplets were provided and by adding initiator (BPO) into the reactor, polymerization reaction of comonomers was initiated and continued until completion.

### Preparation of modified nano-alumina

Adsorption of oleic acid onto the surface of alumina nanoparticles through electrostatic interaction and hydrogen bonding formation was confirmed by FT-IR spectroscopy. FT-IR spectrum of pure alumina, oleic acid and coated alumina with oleic acid (m-nano  $\text{Al}_2\text{O}_3$ ) has been given in Fig. 1. The comparison between FT-IR spectra of alumina and m-nano  $\text{Al}_2\text{O}_3$  reveals the presence of oleic acid characteristic peaks in the pretreated alumina spectra. Before taking FT-IR spectra,



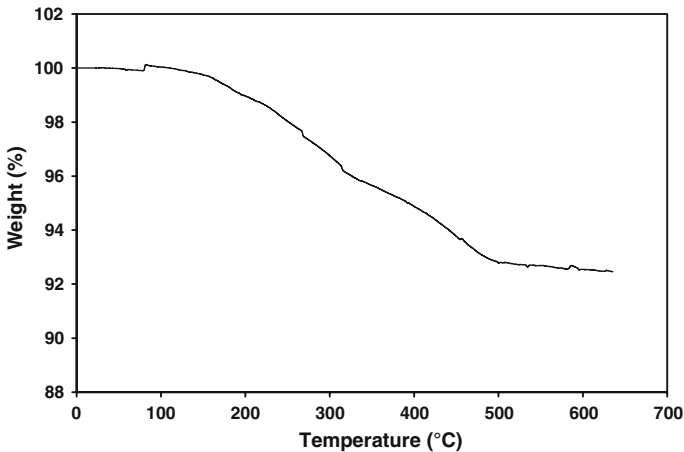
**Fig. 1** FT-IR spectrum of nano- $\text{Al}_2\text{O}_3$  (a), oleic acid (b) and m-nano  $\text{Al}_2\text{O}_3$  (c)

the m-nano  $\text{Al}_2\text{O}_3$  powder was dispersed in methanol (95%) by using ultrasonic bath and then filtered off and dried at  $50\text{ }^\circ\text{C}$  for 10 h. This ensured us about disappearance of any non-adsorbed oleic acid from the surface of alumina nanoparticles. The presence of peak at  $1,708\text{ cm}^{-1}$  (C=O bond) and the stretching C–H bonds at  $3,000\text{--}3,200\text{ cm}^{-1}$  confirms the adsorption of oleic acid onto the alumina nanoparticles.

Also the amount of adsorbed oleic acid onto the surface of alumina nanoparticles was determined by TGA (Fig. 2). 7.5% weight loss at up to  $650\text{ }^\circ\text{C}$  reveals the total amount of oleic acid in obtained product at this step.

#### Determination of alumina content

TGA thermograms were used to determine the amount of nano-alumina encapsulated in the copolymer. For providing samples, latexes were coagulated with few droplets of concentrated sulfuric acid. The coagulum was filtered off and washed three times with plenty of distilled water in order to remove the adsorbed surfactant and sulfuric acid. Then the samples were dried at  $60\text{ }^\circ\text{C}$  for an overnight. This procedure has the advantage of separation of freely dispersed alumina in the latex from the encapsulated ones. So, the residual weight percent after disappearance of the organic polymer at  $650\text{ }^\circ\text{C}$  could be considered as the encapsulated alumina nanoparticles. In order to exclude the probability of formation of non-volatile oxidative degradation products that causes some uncertainties in our calculations, TGA analysis were carried out under  $\text{N}_2$  atmosphere.



**Fig. 2** TGA thermogram of m-nano Al<sub>2</sub>O<sub>3</sub>

The results of corrected weight percent of remained alumina and ultimate percent of encapsulated alumina in the polymeric phase have been listed in Table 3. It is notable that TGA analysis of the blank sample was recorded in order to find out ash content of the copolymer at 650 °C. This ash content was subtracted from those obtained for other samples in order to determine the alumina content with less uncertainty.

It could be observed that the encapsulation of most of the NanoAl<sub>2</sub>O<sub>3</sub> has been done successfully for modified samples and also for non-coated alumina in SMA-1 and SMA-2 samples. Some coagulation was observed at the bottom of reactor vessel for SMA-3 and SMA-4. On the other hand, this coagulation was not observed for the modified nano-alumina particles in which the presence of oleic acid helps in formation of better and more stable dispersion of alumina nanoparticles in the aqueous phase.

Through ICP analysis, the amount of non-encapsulated alumina (freely dispersed alumina in the continuous phase) during miniemulsion polymerization was measured. This could give us a good estimate of the encapsulated alumina indirectly. Preparation of the samples was performed by coagulation of the latex with concentrated sulfuric acid. The remaining serum was used as the source for injection into the ICP. As shown in Table 4, the amount of free alumina in the serum phase is not very significant and this could ensure us about the progress of miniemulsion polymerization on the surface of alumina nanoparticles. It was found that the amount of non-encapsulated alumina for the samples containing modified alumina was less than that of bare alumina.

The added alumina could be found in three different zones: (a) in the coagulated mass because of the aggregation process; (b) as freely dispersed particles, which have not been encountered in the polymeric particles in the miniemulsion polymerization (obtained from ICP) and (c) as encapsulated particles by the newly formed copolymer (obtained from TGA). The difference between total added alumina and the obtained data from TGA and ICP analysis could give a reasonable

**Table 3** TGA analysis for determination of encapsulated nano- alumina

Sample	Added nano-alumina (wt%) <sup>a</sup>	Residue (wt%) <sup>b</sup>	Obtained nano-alumina (wt%) <sup>a</sup>	Encapsulation efficiency (wt%) <sup>c</sup>
Blank	0	1.4	0	0
SMA-1	5	6.2	4.8	96.0
SMA-2	10	10.9	9.5	95.0
SMA-3	15	13.4	12.0	80.0
SMA-4	20	16.9	15.5	77.5
m-SMA-1	5 <sup>d</sup>	6.3	4.6	98.4
m-SMA-1	10 <sup>d</sup>	11.1	9.0	97.2
m-SMA-3	15 <sup>d</sup>	16.0	13.5	97.6
m-SMA-4	20 <sup>d</sup>	20.0	17.2	93.0

<sup>a</sup> Weight percent relative to the total amount of monomers

<sup>b</sup> Weight percent obtained at 650 °C from TGA

<sup>c</sup> Relative to the added nano-alumina or modified nano-alumina

<sup>d</sup> Added amount of modified nano-alumina

**Table 4** ICP analysis for determination of freely dispersed alumina in the continuous phase

Sample	Measured amount of Al in the serum (ppm)	Initial amount of Al (ppm) <sup>a</sup>	Amount of non-encapsulated Al (wt%)
SMA-1	87.7	4,566	1.92
SMA-2	168.4	8,634	1.95
SMA-3	325.9	12,393	2.63
SMA-4	321.6	15,999	2.01
m-SMA-1	67.58	4,223.55	1.60
m-SMA-1	153.06	7,986.45	1.92
m-SMA-3	203.57	11,463.53	1.78
m-SMA-4	302.38	14,799.08	2.04

<sup>a</sup> Theoretical amount added in the procedure

**Table 5** Determination of nano-alumina in different zones

Sample	Encapsulated alumina (wt%) <sup>a</sup>	Non-encapsulated alumina (wt%) <sup>b</sup>	Coagulated alumina (wt%)
SMA-1	96.0	1.92	2.08
SMA-2	95.0	1.95	3.05
SMA-3	80.0	2.63	17.37
SMA-4	77.5	2.01	20.49
m-SMA-1	98.4	1.60	0.0
m-SMA-1	97.2	1.92	0.88
m-SMA-3	97.6	1.78	0.62
m-SMA-4	93.0	2.04	4.96

<sup>a</sup> Obtained from TGA analysis

<sup>b</sup> Obtained from ICP analysis

estimation of entrapped alumina in the coagulum (Table 5). The experimental results show that for both types of the above samples, the percentage of encapsulation decreases with increasing alumina content. This would be concluded that most of the modified nano-alumina is encapsulated and their presence in the



**Table 6** Mean particle sizes obtained from DLS analysis in the latex

Sample	Added nano-alumina (wt%) <sup>a</sup>	Diameter (nm)
Blank	0	70
SMA-1	5	49
SMA-2	10	56
SMA-3	15	61
SMA-4	20	68
m-SMA-1	5 <sup>b</sup>	84
m-SMA-1	10 <sup>b</sup>	119
m-SMA-3	15 <sup>b</sup>	133
m-SMA-4	20 <sup>b</sup>	155

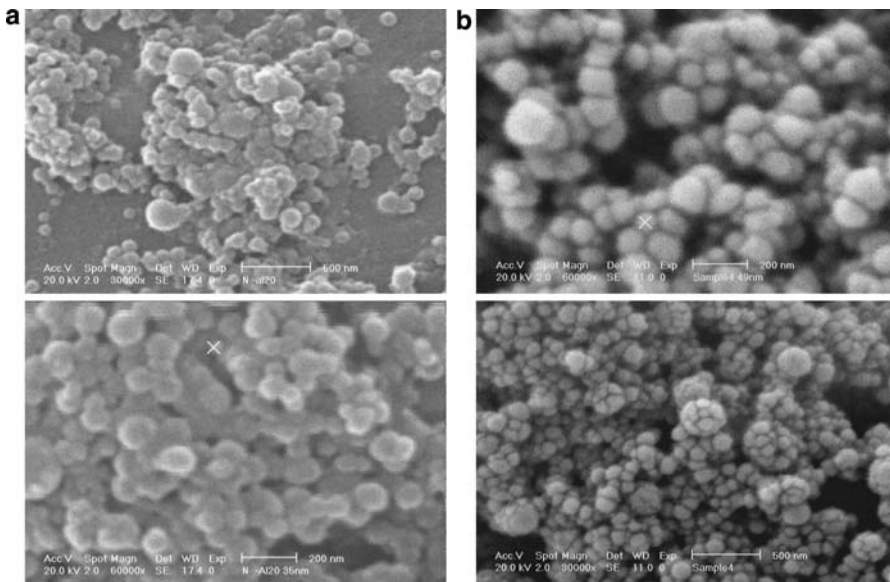
<sup>a</sup> Weight percent relative to the total amount of monomers

<sup>b</sup> Added amount of modified nano-alumina

coagulum is negligible. But for the bare alumina, the amount of nano-alumina in the coagulum is moderate and increases with its amount in the feed.

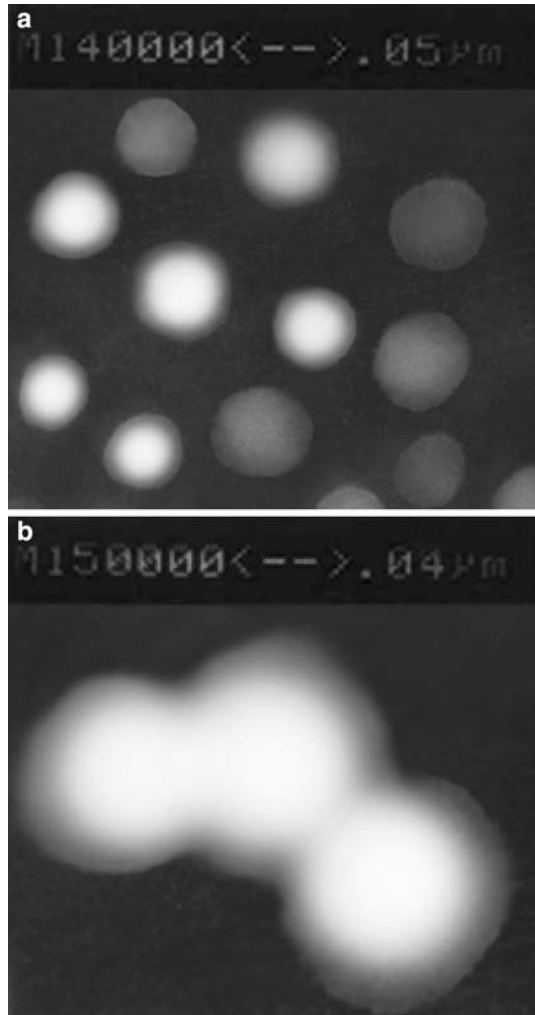
#### Determination of size and morphology of the obtained nanoparticles

Dynamic laser light scattering analysis was used in order to determine mean particles size in the latex. As shown in Table 6, the increase in nanocomposite particle sizes relative to the primary alumina particles (40–47 nm) represents the reason of polymeric shell formation on the inorganic cores. This illustrates that the polymerization reaction have certainly progressed in the presence and on the surface



**Fig. 3** a SEM micrograph of copoly (St-MMA)/nano- $\text{Al}_2\text{O}_3$  (20 wt%) with different magnifications. b SEM micrograph of copoly (St-MMA)/m-nano- $\text{Al}_2\text{O}_3$  (20 wt%) with different magnifications

**Fig. 4** **a** TEM micrograph of copoly (St–MMA)/nano- $\text{Al}_2\text{O}_3$  (20 wt%) (the scale is 0.05  $\mu\text{m}$ ). **b** TEM micrograph of copoly (St–MMA)/m-nano  $\text{Al}_2\text{O}_3$  (20 wt%) (the scale is 0.04  $\mu\text{m}$ )



of alumina nanoparticles. Another important result is the role of alumina as seed or primary nanoparticles and the polymerization conditions do not allow nanocomposite particles to grow up too much. In fact, obtaining such nanoparticles is the result of miniemulsion polymerization condition that controls the growth and size of particles.

The growth of particle diameter in the presence of modified alumina was due to the aggregation of primary m-nano  $\text{Al}_2\text{O}_3$  nanoparticles, which was related to the presence of oleic acid. Oleic acid was not able to stabilize each particle separately through steric effects in the polymerization condition and consequently, they tended to aggregate to the larger ones. Therefore, these aggregates become the core for adsorption of monomer and polymerization reaction to reach to core-shell nanocomposite particles and dispersion stability with semi-spherical particles.

The morphology of the above nanocomposite particles was examined by TEM and SEM too. SEM analysis reveals the formation of spherical shape of the core/shell nanoparticles with smooth outer surface (Fig. 3). TEM micrographs show dark nano-alumina cores and light polymeric shells around each core (Fig. 4).

## Conclusion

Alumina particles with nanometric size were encapsulated by copoly (St/MMA) via miniemulsion polymerization process. Polar interactions between the surfactant used to stabilize nano-alumina particles within the comonomer mixture and produce stable miniemulsion. Ultrasonic irradiation has an excellent dispersion effect on the modified alumina with oleic acid in the aqueous media containing surfactants relative to the bare nano-alumina. The stable copoly (St/MMA)/alumina nanocomposite latexes with high monomer conversion and medium solid content were prepared through ultrasonic assisted miniemulsion polymerization in the presence of alumina. The obtained nanocomposite particles were analyzed by different techniques such as DLS, SEM and TEM in order to prove the morphology and size of the particles. Also the probability of presence of primary dispersed nano-alumina in different zones was determined through TGA and ICP measurements.

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