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Preparation of poly (styrene–methyl methacrylate)/SiO_2 composite nanoparticles via emulsion polymerization. An investigation into the compatiblization

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Abstract

Inorganic/organic nanocomposite systems, in which inorganic particles are encapsulated into the polymer matrix, are new classes of polymeric materials. These materials combine the properties of both components. It means that polymer component with excellent optical property, flexibility and toughness could improve the brittleness of inorganic particles and besides, inorganic particles could increase the strength and modulus of polymers. There are various methods to make these inorganic/organic nanocomposites. One of them is the chemical process, in which polymerization is performed directly in the presence of the inorganic particles. Examples of miniemulsion, suspension or dispersion polymerization can be found in the literature but emulsion polymerization is by far the technique most frequently used.

In this work, latex containing nanostructure hybrid of copolymer (styrene, methyl methacrylate, acrylic acid) and inorganic nanoparticles (silica) with core/shell structure was prepared via semi-batch emulsion polymerization. At first, silica nanoparticles were dispersed in water phase in an ultrasound bath to prevent the aggregation of nanoparticles, and then emulsion polymerization was performed in the presence of silica nanoparticles. Related tests and analysis confirmed the success in synthesis of nanostructure hybrids. Induced coupled plasma (ICP) analysis and thermal gravimetric analysis (TGA) showed the presence and amount of silica nanoparticles in the final latex. Dynamic light scattering (DLS) analysis confirmed the presence of 25–35 nm particles in the system and transmission electron microscopy (TEM) showed the core/shell morphology of nanoparticles. It has been shown that with an appropriate surfactant, adjusting the pH of media, using suitable monomers and under controlled conditions, it would be possible to produce stable organic/inorganic composite nanoparticles with core/shell structure. In another attempt and in order to investigate the effect of compatiblizing system, styrene–methyl methacrylate was copolymerized in the presence of modified silica particles with oleic acid as the inorganic dispersed phase at the same condition. Similar characterizations were performed in order to have a worthwhile comparison. The results for the late procedure show the effect of oleic acid in formation of aggregates as the core for polymeric nanocomposite particles.

Keywords: Emulsion polymerization; Nanoparticle; Silica; Styrene; Methyl methacrylate

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1. Introduction

Preparation of nanoparticles is one of the most important topics in nanotechnology [1]. Inorganic/organic composite nanoparticles are of great interest, as they are expected to have combined properties of both inorganic nanoparticles and organic molecules [2].

Preparation of composite particles by the encapsulation of inorganic particles by polymers through polymerization is an efficient way to prevent their agglomeration and improve the mechanical properties. Among them, encapsulation of silica [3–5] has been extensively studied before.

In recent years, organic-inorganic hybrid nanomaterials have attracted much interest because of their extensive potential applications in various fields of material science, ranging from paints, magnetic fluids, and high-quality paper coating to catalysis, microelectronics, and biotechnology [6].

Organic polymer materials with excellent optical properties, good flexibility and toughness are easy to process, and can improve the brittleness of inorganic materials. On the other hand, inorganic materials can improve the strength of polymers. Organic–inorganic composites combine advantages of both polymer and inorganic materials [7].

Organic–inorganic nanocomposites can be prepared by directly mixing nanoparticles with organic compounds or by a sol–gel process. Commonly used inorganic nanoparticles include SiO_2, TiO_2, ZnO, etc. Nano-SiO_2 has been studied in many polymer systems [8–13], such as poly (methyl methacrylate) [8], polystyrene [9], polypropylene [10], acrylic based polyurethane [11], and poly (2-hydroxyethyl methacrylate) [12].

Heterogeneous polymerization, especially emulsion polymerization, provides an effective way of synthesizing nanoparticles with various architectures and forms [6]. Seeded emulsion polymerization technology is commonly used in the production of emulsion, that is, the seeded emulsion polymerization occurs beforehand in the presence of water, emulsifier, waterborne initiator and a small amount of monomer, in which the emulsion has a large number of particles with very small size. Then the polymerization reaction continues in the presence of the seeded emulsion, water, emulsifier, initiator and monomer. This method can control the reaction rate, particle size and morphology effectively [7].

Several patents [14,15] and papers deal with the encapsulation of colloidal metals [16], sol–gel type metal oxide particles (SiO_2, TiO_2) and other inorganic pigments [17] to give organic–inorganic hybrid dispersions, where the polymer shell is built in situ by means of conventional emulsion [18,19], miniemulsion [20,21] and related dispersed-phase polymerization processes. When the hydrophobic coat layer is simply adsorbed on the hydrophilic inorganic particle surface, as with non-ionic surfactants [22], amphiphilic polymers [23] or hydroxypropyl cellulose [24], the poor chemical interaction between the three phases (inorganic–hydrophobic–organic polymer) can result in desorption of the shell-forming organic polymer, while pH and ionic strength are changed. Since the encapsulant in these organic–inorganic hybrids is an organic polymer, the core inorganic particle usually presents a more hydrophilic surface. Therefore, either the adsorption of the polymerization initiator onto the particle surface through electrostatic interaction [25] or special polymerization techniques are generally required when polymerization onto an unmodified (i.e. not hydrophobically modified by surface-graft reaction) seed inorganic particle is carried out by conventional emulsion process.

Chemical modification of silica particles surface with a reactive coupling agent has been employed for the synthesis of hybrids by subsequent emulsion polymerization of hydrophobic vinyl monomers, such as acrylates and styrene [26,27].

The anchoring monomer can also be simply adsorbed on the silica particle surface [19]. Yang et al. [28] had prepared particles of silica encapsulated with polymer by phase-inversion emulsification. Atom transfer radical polymerization (ATRP) [29] was also used to prepare monodisperse polymer-coated inorganic seed nanoparticles.

For the first time, Ding et al. [30] used oleic acid as functionalized monomer because the C=C bonds of oleic acid can be copolymerized with styrene monomer. They reported oleic acid could bond to the silica surface with a single hydrogen bonding. The surface-modified silica nanoparticles were then used in the encapsulation process. Styrene monomer, added to fully dispersed silica particles modified by oleic acid used as seeds, was copolymerized with the oleic acid via in situ emulsion polymerization, in the presence of an initiator. It has been proven that this method is useful to obtain narrowly distributed particles with well-defined particle morphology.

The aim of this work is to prepare styrene–methyl methacrylate/modified nano-SiO_2 composite particles with core–shell morphology by using of modified nano-SiO_2 as seeds; and to investigate the effect of level of nano-SiO_2 on the size, morphology and yield of encapsulation process through emulsion polymerization reaction. In fact, the effect of oleic acid and an auxiliary monomer (acrylic acid) on controlling the efficiency of this process was studied.

2. Experimental

2.1. Materials

Styrene (St) 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. Acrylic acid (AA) from BASF, methyl methacrylate (MMA), oleic acid and ammonium persulfate (APS) from Merck Chemical Co., sodium dodecyl sulphonate (SDS) from Aldrich, nano-SiO_2 (Sil) with commercial name of Aerosil 200 (nanoparticle size of 12 nm) from Degussa, and sodium bicarbonate ($NaHCO_3$) were used without further purification.

2.2. Equipments

TGA thermograms were recorded on a STA-PL instrument from England. The essential operations were carried out according to the manufacturer's instructions. The samples were weighed on a Shimadzu LIBRORE AEU-210 analytical electrobalance to an accuracy of 0.0001gr for this analysis. FT-IR spectrum was recorded on a FT-IR BRUKER-IFS 48 spectrophotometer (Germany) using KBr pellet. Size of the particles was measured by a SEMATECH light scattering (France) with 633 nm wavelength. TEM micrographs were taken by a ZEISS 902A (Germany). The samples were diluted up to 20 times, stained with OsO_4 and dropped on a copper grid for TEM analysis. Silica dispersions were prepared in a Julabo Labortechnik GMBH D-733 Seelbach (Germany) ultrasound bath with frequency of 5 kHz.

2.3. Modification of nano-SiO_2 by oleic acid

Nano-SiO_2 was modified with oleic acid. Aerosil 200 (6.3 g) was firstly dispersed into 90 ml distillated water with the aid of ultrasound bath for 3 h. Then 1.5 ml oleic acid was added into the dispersion and was vigorously stirred for 90 min at room temperature with a magnetic stirrer.

Afterwards, 5 ml of 25 wt.% aqueous ammonia solution was added into the solution and the agitation was continued for an overnight. Then the dispersion was neutralized with 30 wt.% aqueous HCl solution. The mixture was centrifuged (2500 rpm) for 30 min and the obtained precipitates were washed three times with 15 ml 1/1 ethanol/water (V/V) solution to remove the excess amount of oleic acid. The resulting precipitates were dried in oven at 50 °C for 24 h to yield 4.33 g modified nano-SiO_2 (m-Sil) powders.

2.4. Encapsulation of SiO_2 via emulsion polymerization

St-MMA-AA monomers with molar ratios of 2:0.9:0.1 and St-MMA monomers with molar ratio of 2:1 were polymerized isothermally by semi-batch emulsion copolymerization in a 500 ml four necked round bottomed glass reactor, which was equipped with a reflux condenser, a mechanical stirrer, a dropping funnel, and a nitrogen gas inlet for preparation of Sil and m-Sil containing latexes respectively.

In a typical synthesis, 2.5 g modified nano-SiO_2 powders was dispersed into 20 ml distilled water with the aid of ultrasound bath for 2 h. Styrene (18.8 ml) and 8.6 ml methyl methacrylate were premixed and poured into the dropping funnel. The initiator (APS) was dissolved in a definite amount of distilled water, and then the buffer solution of $NaHCO_3$ and surfactant (SDS) were added. The above solution was moved into the reactor vessel. The reaction vessel was charged with modified nano-SiO_2 dispersion. The initial charge was stirred at 300 rpm and heated up to 75 °C. Afterwards, the monomers were fed into the reactor in a separate stream with constant flow rates slow enough to reach monomer starved conditions. The time of feeding was 75 min and after addition of the monomers, the content was stirred for an additional 4 h. Then, the system was cooled to room temperature and the final latex was obtained without any post preparative treatments. This procedure was also applied for preparation of nano-SiO_2 containing latex. A detailed recipe given in Tables 1 and 2 summarizes a series of encapsulation experiments.

3. Result and discussion

3.1. FT-IR analysis

Surface modification of nano-SiO_2 (Sil) particles was performed with oleic acid through electrostatic interactions and hydrogen bonding formation.

Table 1
A Typical recipe used for the encapsulation of silica particles through emulsion polymerization

Components	Sil-10	m-Sil-10
Styrene	2 mol	2 mol
Methyl methacrylate	0.9 mol	1 mol
Acrylic acid	0.1 mol	–
Nano-SiO_2	10 wt.%[a]	–
Modified nano-SiO_2	–	10 wt.%[a]
$(NH_4)_2S_2O_8$	1 wt.%[a]	1 wt.%[a]
SDS	3.5 wt.%[a]	3.5 wt.%[a]
$NaHCO_3$	0.2 wt.%[a]	0.2 wt.%[a]
Distilled water	80 wt.%[b]	80 wt.%[b]

[a] Based on the total weight monomers.
[b] Based on the total weight of latex.

Characterization of the obtained modified particles (m-Sil) was carried out by FT-IR spectroscopy. The comparison between FT-IR spectra of Sil and m-Sil reveals the appearance of oleic acid characteristic peaks in the m-Sil spectra after washing with 1:1 ethanol/water solution. This washing ensured us that the obtained modified particles do not contain any unreacted oleic acid. Therefore, the newly appeared peaks in the FT-IR spectrum could be anticipated to the adsorbed oleic acid on the silica particles. Fig. 1 shows the spectra of pure oleic acid (1a), silica (1b) and modified silica (1c) separately.

The presence of stretching C–H bonds of 3145 and 3047 cm^{-1} and the peak at 1716 (C=O bond) confirms the adsorption of oleic acid on nano-silica particles (Fig. 1c).

3.2. Thermal gravimetric analysis

Preparation of the samples for thermogravimetry analysis (TGA) was performed by coagulation of a latex sample with concentrated sulfuric acid. The coagulated sample was filtered off and washed three times with distilled water in order to remove the adsorbed surfactant and H_2SO_4. Then the samples were dried at 60 °C for an overnight. This procedure has the advantage of separation of free dispersed silica (Sil) from the polymeric composite particles in the latex. Hence, the residual weight percent after disappearance of the organic polymer at high temperatures (600 °C) could be considered as the encapsulated silica particles in the obtained nanocomposite particles. 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 in N_2 atmosphere.

The results of corrected weight percent of remained silica and ultimate percent of encapsulated silica in the polymeric phase have been listed in Table 3.

It is notable that TGA of the blank sample was recorded in order to find out ash content of the copolymer at 600 °C. This ash content was subtracted from those obtained for other samples to determine the silica content with less uncertainty. By the way, the results (Table 3) reveal that all of the used silica particles in each recipe were not encapsulated through the copolymerization reaction. A part of this comes from the aggregation phenomena, which occurs during seeded emulsion polymerization and will result in dismissing of the dispersed silica as sediments from the polymerization media. This was less observed for the modified silica particles in which the presence of oleic acid helps in formation of better and more stable dispersion for silica particles in the aqueous phase.

3.3. ICP analysis

Sample preparation for ICP analysis was performed by coagulation of the latex with concentrated sulfuric acid. The remaining serum was used as the sample for injection into the ICP analyzer.

Table 2
Recipes used for preparation of several samples based on silica and modified silica encapsulants[a]

Sample	St	MMA	AA	Sil	m-Sil	APS	SDS	$NaHCO_3$	Water
Sil-B	14.4	6.25	0.5	–	–	0.21	0.795	0.04	84.6
Sil-5	28.77	12.45	1	2.11	–	0.42	1.47	0.08	168.8
Sil-7.5	28.77	12.45	1	3.17	–	0.42	1.47	0.08	168.8
Sil-10	28.77	12.45	1	4.23	–	0.42	1.47	0.08	168.8
Sil-15	21.6	9.35	0.75	4.76	–	0.32	1.1	0.06	126.8
m-Sil-B	16.88	8.11	–	–	–	0.25	0.87	0.05	104
m-Sil-10	16.88	8.11	–	–	2.5	0.25	0.87	0.05	112
m-Sil-12.5	16.88	8.11	–	–	3.125	0.25	0.87	0.05	116
m-Sil-15	16.88	8.11	–	–	3.75	0.25	0.87	0.05	118.4

[a] All reported amounts are in gram.

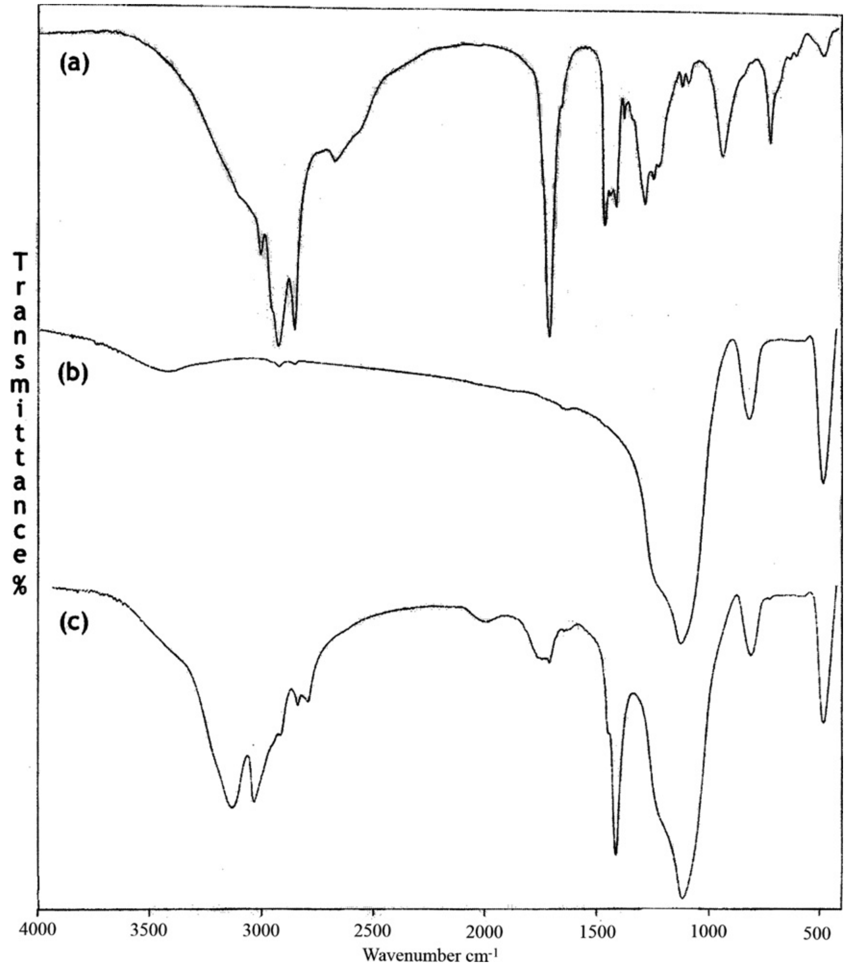

Fig. 1. The spectrum of (a) pure oleic acid, (b) silica and (c) modified silica.

Table 3
The results of TGA analysis for determination of encapsulated silica

Sample	Residue at 600 °C (wt.%)	SiO_2 residues at 600 °C (wt.%)	Amount of encapsulated SiO_2 (wt.%)
Sil-B	0.95	–	–
Sil-5	3.74	2.79	55.8
Sil-10	5.25	4.3	57.4
Sil-15	7.47	6.52	43.5
m-Sil-B	1.2	–	–
m-Sil-5	4.16	2.96	59.3
m-Sil-10	7.84	6.64	66.4
m-Sil-15	14.28	13.8	87.2

Through this preparative method, the amount of non-encapsulated (free) silica during emulsion polymerization was measured. This could give us a good estimation of the encapsulated silica indirectly. The results have been shown in Table 4. It could be observed that the amount of free silica in the serum phase is not very significant and this could ensure us about the progress of emulsion copolymerization on the surface of silica particles.

Also it is notable that for the modified silica samples, the percentage of encapsulation increases with increasing m-Sil content. For unmodified silica samples, the percentage of free silica decreases and then increases. The optimum point for maximum encapsulation is Sil-10. This observation could be explained according to the probability of aggregation of silica particles during emulsion copolymerization at higher silica contents.

As a consequence, the added silica could be found in three zones: (1) coagulated mass because of the aggregation process; (2) dispersed free particles, which have not been encountered as primary seeds in the emulsion copolymerization and (3)

Table 4
The results obtained from ICP analysis for determination of silica content

Samples	Measured amount of silica in the serum (ppm)	Initial amount of silica (ppm)[a]	Amount of non-encapsulated silica (wt.%)
Sil-5	7700	23,333	32.8
Sil-10	13,700	46,666	29.3
Sil-15	25,550	70,000	36.4
m-Sil-5	7400	23,333	31.5
m-Sil-10	11,400	46,666	24.4
m-Sil-15	2200	70,000	3.1

[a] Added in each batch (theoretical).

Table 5
The comparison between ICP and TGA analysis data

Samples	Amount of encapsulated silica (wt.%)[a]	Amount of non-encapsulated silica (wt.%)[b]	Amount of coagulated silica (wt.%)
Sil-5	55.8	32.8	11.4
Sil-10	57.4	29.3	13.3
Sil-15	43.5	36.4	20.1
m-Sil-5	59.3	31.5	9.2
m-Sil-10	66.4	24.4	9.1
m-Sil-15	87.2	3.1	9.7

[a] From TGA analysis.
[b] From ICP analysis.

encapsulated particles by the newly formed copolymer. Table 5 shows a comparison between TGA and ICP results that could give us an estimation of silica amounts in the mentioned zones.

3.4. Determination of particle size and morphology

Dynamic light scattering (DLS) technique was used in order to determine mean particle size in the latex (Table 6). In the case of unmodified silica samples, the blank one (Sil-B) has the maximum particle size. By insertion of silica particles with diameter of 12 nm, the obtained polymeric nanocomposite hybrids reveal the growth of particle size but their diameter is still less than that of the blank sample. This illustrates that the polymerization reaction will progress certainly in the presence and on the surface of silica nanoparticles. Otherwise, their diameter must be around that of Sil-B. Another important result is the role of silica particles as primary seeds and the stability conditions, which do not allow nanocomposite particles to grow up remarkably and remain less than 32 nm. In fact, obtaining nanoparticles is the result of imposed polymerization conditions that controls the growth of particles' diameter.

Table 6
Mean particle sizes obtained from dynamic light scattering analysis

Samples	Particle diameter (nm)
Sil-B	64.1
Sil-5	21.6
Sil-10	30.3
Sil-15	32.3
m-Sil-B	95.3
m-Sil-5	100.3
m-Sil-10	144.6
m-Sil-15	199

TEM micrographs of the stained polymeric particles with OsO_4 shows dark SiO_2 cores and lighter polymeric shells around each core (Fig. 2) that confirms our illustration about formation of such core–shell nanoparticles obviously.

The results for modified silica particles were somewhat different. That is, the blank sample without any silica had smaller particle size rather than those containing modified silica particles. Of course, the difference between particle size of Sil-B and m-Sil-B comes from the difference in monomer composition in the recipe. In other words, AA acts as a water soluble monomer that controls polymerization reaction through homogeneous nucleation, while this mechanism could change to micellar nucleation in the absence of AA and resulting in the larger particles probably.

The growth of particle diameter in the presence of modified silica was due to the aggregation of primary seed particles, 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 agglomerate (aggregate) to larger ones. Therefore, these aggregates become the core for adsorption polymerization reaction to reach dispersion stability. Hence, the growth in nanocomposite particles' diameter was observed and it was proven by their TEM micrograph (Fig. 3). Morphology of the particles reveals that the modified silica aggregates act as the core for deposition of the copolymer in the shell.

Consequently, it could be considered that there are two mechanisms in formation of nanocomposites via using oleic acid:

(a) Oleic acid modifies each silica nanoparticle separately, and then the aggregates of modified silica nanoparticles are encapsulated during polymerization reaction.

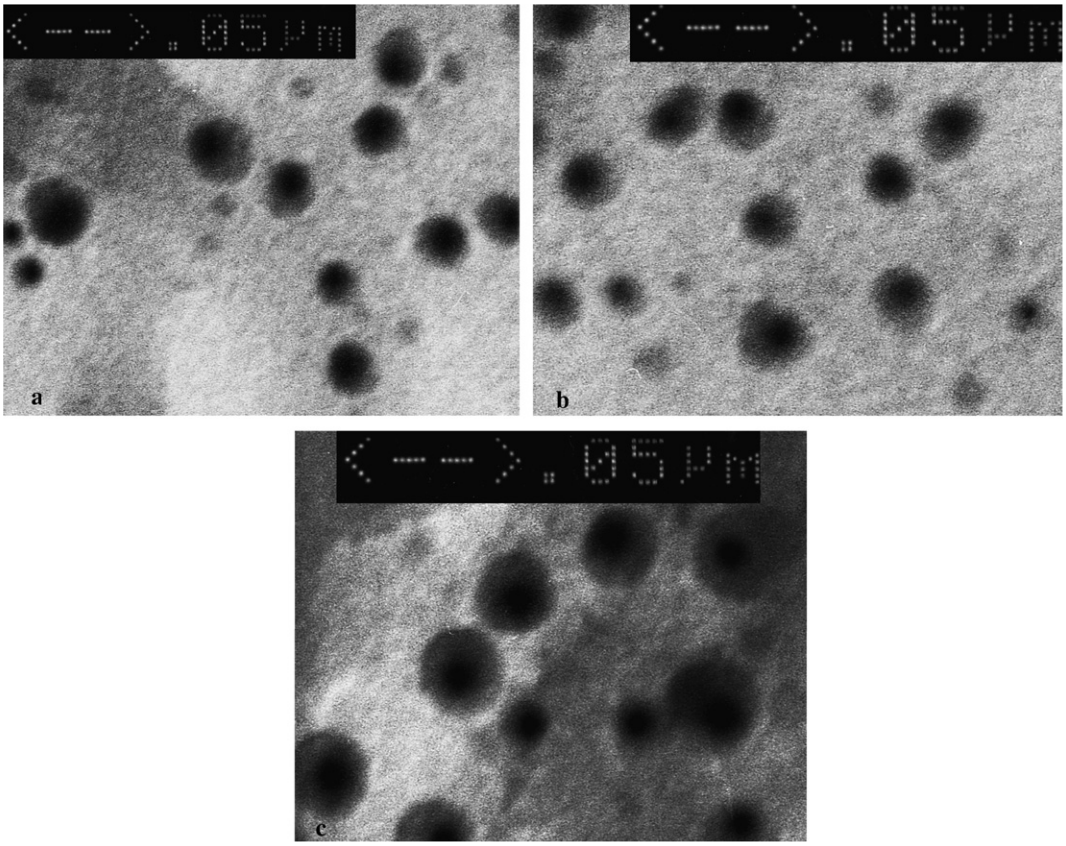

Fig. 2. TEM micrograph of (a) Sil-5 sample, (b) Sil-10 sample and (c) Sil-15.

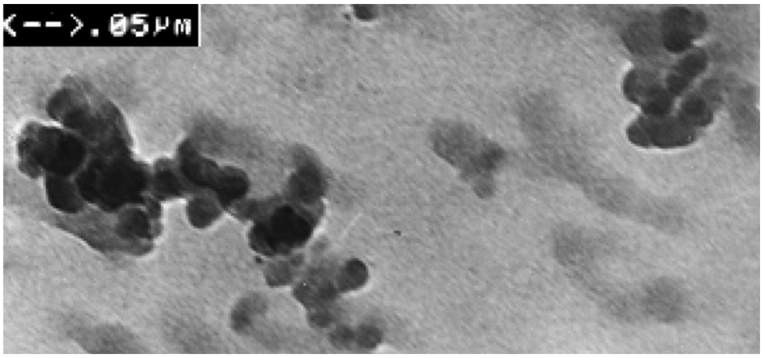

Fig. 3. TEM micrograph of m-Sil-5 sample.

(b) Silica nanoparticles aggregate before modification with oleic acid and then these aggregates will be modified with oleic acid and finally the polymerization reaction will proceed in the presence of these modified aggregates.

Hence, the aggregation process will take place during either encapsulation with the polymer [path (a)] or modification with oleic acid [path (b)]. The evidence prove that path (b) is more probable, because if path (a) was the predominant one and at least some single modified silica nanoparticles encapsulated with core–shell structure (less than 50 nm) should be observed in TEM micrographs. This would lead to a bimodal particle size distribution (from DLS analysis). Due to the lack of such observations, path (b) was chosen for taking such particles.

3.5. Particle formation mechanism

The mechanism for emulsion polymerization giving organic-inorganic hybrids with core–shell structure is almost complicated, especially in the case that the particles would be in nanoscale. There are several parameters controlling morphology of the particles and their dispersion stability in the system.

Here, we considered two cases that may affect on the morphology and stability with respect to the pH of latex.

Silica nanoparticles were dispersed in the water phase barely with the aid of ultrasonic waves primarily. In order to absorb ionic surfactant on the silica surface, it was necessary to control pH by using of the buffer ($NaHCO_3$). Nano-silica particles (Aerosil 200) have a pH of 3.7–4.7 in the aqueous dispersion, which shows their acidic characteristics. This facilitates the adsorption of anionic surfactant through dipolar interactions and hydrogen bonding formation. It is noteworthy that in the case of non-acidic media, the polymerization reaction will proceed mainly in the empty micelles (without any silica particles) due to the self-aggregation of surfactant molecules. Then the polymerization rate will be faster (exceeds up) and the obtained polymer has no role in the stabilization of the dispersed silica particles. Therefore, the acidic media favors the formation of admicelles (bilayered surfactants) on the nanoparticles' surface, in which emulsion polymerization takes place by entering oligoradicals into them [31]. This makes the nano-silica particles be encapsulated by newly forming polymer and will result in creation of core–shell morphology of the final particles. As a result, the nano-silica dispersion will be stable enough and the coated polymeric shell prevents their aggregation (agglomeration).

Of course, there are two competing criteria for progress of polymerization reaction: (i) in the above mentioned admicelles and (ii) in the micelles formed by surfactants (without any silica particles). It is a correct assumption that the major loci for emulsion polymerization would be in the admicelles due to the large surface area of silica particles and consequently admicelles have priority over the conventional micelles for leading to the observed core–shell morphology.

4. Conclusions

In this work, latex containing nanostructure hybrid of copolymer (styrene, methyl methacrylate, acrylic acid) and inorganic nanoparticles (silica) with core/shell structure was prepared via semi-batch emulsion polymerization. At first, silica nanoparticles were dispersed in water phase by ultrasonication to prevent aggregation of nanoparticles, and then seeded emulsion polymerization was performed in the presence of silica nanoparticles. Related tests and analysis confirmed the success in synthesis of nanostructure hybrids. Also it is notable that for the modified silica samples with oleic acid, the percentage of encapsulation increases with increasing silica content. For unmodified silica samples, the percentage of free silica decreases and then increases. The optimum point for maximum encapsulation was found at this condition. This observation could be explained according to the probability of aggregation of silica particles during emulsion copolymerization at higher silica contents. As a consequence, the added silica could be found in three zones: (1) coagulated mass because of the aggregation process; (2) dispersed free particles, which have not been encountered as primary seeds in the emulsion copolymerization and (3) encapsulated particles by the newly formed copolymer.

Dynamic light scattering analysis confirmed the presence of nano-sized particles in the system and TEM micrographs showed the core/shell morphology of nanoparticles. This illustrates that the polymerization reaction will progress certainly in the presence and on the surface of silica nanoparticles. These results for modified silica particles were somewhat different from that of bare silica. The growth of particle diameter in the presence of modified silica was due to the aggregation of primary seed particles, which was related to the presence of oleic acid. However, this growth for the bare silica particles was less and almost each composite nanoparticle contained one silica particle.

It has been shown that with an appropriate surfactant, adjusting the pH of media, using suitable monomers and under controlled conditions, it would be possible to produce stable organic/inorganic composite nanoparticles with core/shell structure. In other words, the effect of compatiblizing system, acrylic acid or oleic acid, on the loading density, morphology and particle size was investigated.

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