



# Silica encapsulation by miniemulsion polymerization: A novel approach of efficient chemical functionalization on silica nanoparticles



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## ABSTRACT

Hybrid latex particles with core-shell nanostructure were prepared via miniemulsion polymerization. Copolymer of (methyl methacrylate-butyl acrylate-methacrylic acid) was formed the shell on the surface of modified SiO<sub>2</sub> nanoparticles as the core. In order to create compatibility between inorganic and polymeric phases, modification of SiO<sub>2</sub> nanoparticles was performed with methylene diphenyl diisocyanate and 2-hydroxy ethyl methacrylate with an optimized procedure for the first time, and then miniemulsion polymerization was carried out in the presence of modified SiO<sub>2</sub>. The products of each step were characterized. The results of DLS, TEM and SEM analyses proved the formation of encapsulated hybrid latex particles. DLS and SEM data revealed that the sizes of nanocomposite particles vary between 60 and 120 nm for 0–10 wt% of the modified SiO<sub>2</sub> nanoparticles. Thermal stability and thermo-mechanical properties of the obtained nanocomposite films were studied by TGA and DMTA, respectively. It was found that the best improvement of properties is achieved for nanocomposite containing 7 wt% modified silica nanoparticles.

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## 1. Introduction

Inorganic/organic composite nanoparticles are of great interest, as they are expected to have combined properties of both inorganic and organic ingredients. Preparation of composite materials via encapsulation of inorganic particles by polymers is an efficient way to prevent the agglomeration of inorganic nanoparticles and to improve thermo-mechanical properties of prepared nanocomposites. Several patents [1,2] and papers deal with the encapsulation of colloidal metals, sol–gel type metal oxide particles (SiO<sub>2</sub>, TiO<sub>2</sub>) and other inorganic pigments [3–5] to give organic–inorganic hybrid dispersions, where the polymer shell is built in situ by means of conventional emulsion [3], seeded emulsion [6], miniemulsion [7] and related dispersed-phase polymerization processes [8].

When considering different synthetic approaches to

nanocomposite materials, miniemulsion polymerization is known as a convenient and powerful technique to encapsulate a wide range of different inorganic nanoparticles [9]. In this method, the droplets loaded with inorganic particles ideally stay constant in size and shape. They can directly be transformed into polymer particles, while acting as “nanoreactors” [10]. To synthesis nanocomposite particles with great encapsulation efficiency, the inorganic particles should be well dispersed in the monomer prior to emulsification. Inorganic particles may disperse homogeneously in the organic phase when they are surface modified by appropriate modifiers [11].

Among different inorganic nanoparticles, silica is one of the most attractive one with several favorable advantages such as relatively inexpensive, nontoxic, biocompatible, high thermal resistant and especially its ability to reinforce polymer matrix's mechanical properties [12]. Therefore, SiO<sub>2</sub> is the most frequently used nanoparticle for fabrication of polymer nanocomposites [13]. As a matter of fact, however, the preparation of polymer/SiO<sub>2</sub> nanocomposites via miniemulsion polymerization method is not that easy. This is because of the hydrophilic nature of silica nanoparticles that is not compatible with hydrophobic polymers. The incompatibility, will result in bad dispersion of nanoparticles and

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poor interfacial interaction between the two components.

In order to circumvent the inherent incompatibility of polymers and silica, it is necessary to modify the surface of this inorganic material [12,14–16]. To establish a thermochemical or chemical link at the interface of the organic and inorganic constituents, different modification methods such as physical modification using surfactant [17], chemical modification using coupling agents [18,19] or grafting polymer chains [20,21] have been used extensively. One major approach of covalent functionalization of silica particles was employing alkoxy silane compounds. Through the condensation reaction between the silanol groups (Si–OH) of the silica surface and the alkoxy silane compounds, organic functional groups are introduced onto the surface of silica nanoparticles and the hydrophilic nature of SiO<sub>2</sub> nanoparticles altered to hydrophobic [11,22]. However, some drawbacks accompanied by this reaction route. For example, some silanol groups of the alkoxy silane compounds might remain in the product owing to the incompleteness of the dehydration reaction. These silanol groups were highly reactive and might cause further condensation reactions during the period of storage and usage of the formed nanocomposites [23]. Such unwanted reactions of alkoxy silane molecules could change the properties of the nanocomposite (like glass transition temperature) [14]. In addition to the all mentioned drawbacks, the high cost of the alkoxy silane compounds limited their practicability in mass production. Therefore, the development of novel strategies that could overcome some of these drawbacks is highly desirable. In order to reach this aim, different chemical compounds are used as alternative surface modifiers for alkoxy silanes. For example it has been demonstrated that diisocyanate based molecules such as methylene diphenyl diisocyanate (MDI) could be used as surface modifier of silica nanoparticles [24]. However, such a modification process did not establish unsaturated bonds on the surface of silica nanoparticles. Unsaturated bonds could be used for grafting polymeric chains to the silica nanoparticles through radical polymerization process and fabricate a nanocomposite with an enhanced physico-mechanical properties [14].

The present study therefore focuses on seeking a practical and efficient approach to functionalize the surface of silica nanoparticles in a way that compensates the mentioned drawbacks. Here, methylene diphenyl diisocyanate (MDI) and 2-hydroxy ethyl methacrylate (HEMA) were utilized as surface modifiers for silica nanoparticles. The modified silica nanoparticles were encapsulated with acrylic polymer through miniemulsion polymerization. Such a modification process, introduced covalent bonds between polymer shell and silica nanoparticles and did not employ alkoxy silane compounds and sol–gel process in the preparation process, consequently to overcome the drawbacks found in the reported literatures (e.g. high cost and unwanted reactions) [17,23]. Acrylic/silica nanocomposite with superior thermal stability and thermo-mechanical properties were obtained.

## 2. Experimental

### 2.1. Materials

Monomers, methyl methacrylate (MMA) from Merck Chemical Co., butyl acrylate (BuA) from Fluka, methacrylic acid (MAA) from BASF, Methylene diphenyl diisocyanate (MDI) and 2-hydroxyethyl methacrylate (HEMA) from Aldrich were purchased and used as received. Sodium dodecyl sulfate (SDS) and Triton X-100 from Aldrich, Ammonium persulphate (APS) from Fluka, sodium bicarbonate (NaHCO<sub>3</sub>) and hexadecane (HD) from Merck Chemical Co., were used without any further purification. Fumed silica nanoparticles (SiO<sub>2</sub>) with commercial name of Aerosil 200 (average particle size of 12 nm and specific surface area (Brunauer, Emmett

and Teller (BET) analysis) of 200 m<sup>2</sup> g<sup>-1</sup>) were supplied by Degussa. Deionized (DI) water was used in all recipes. Hydroquinone (Aldrich) was used for stopping the reaction in the samples withdrawn from the reactor.

### 2.2. Characterization

TGA thermograms were recorded on a STA-PL instrument from England. The essential operations were carried out according to the manufacturer's instruction. FT-IR spectrum was recorded on a FT-IR BRUKER-IFS 48 spectrophotometer (Germany) using KBr pellet. Mean particle size was measured by SEMATECH light scattering (Nice, France) with 633 nm wavelength. Size and morphology of the samples were also investigated by scanning electron microscopy (SEM) with Vega II instrument from Tescan (The Czech Republic). A drop of the negative stained latex was placed on the sample holder and dried. They were then put under vacuum, flushed with argon (Ar), evacuated, and sputter-coated with gold for SEM analysis. TEM micrographs were taken by a CEM 902A ZEISS transmission electron microscope with an accelerating voltage of 80 keV (Oberkochen, Germany). For the TEM and SEM analyses, a negative staining technique was applied to obtain high quality results. Hence, 0.5 mL of 2 wt% phosphotungstic acid (PTA) aqueous solution was added to 2 mL of the diluted latex to 1 wt% (solid content) prior to drying on the holder. Then the samples were dried at room temperature for 24 h. Dynamic mechanical thermal analysis (DMTA) was performed using Triton 2000 DMA (Triton Technology Co. England).

### 2.3. Preparation of modified SiO<sub>2</sub> nanoparticles (MH-SiO<sub>2</sub>)

The modification process was performed in two stages. At first, silica (4.0 g) was dispersed in toluene (200 mL) by sonication (Bandelin, HD3200, probe KE-76, power 70 W) for 30 min. To avoid heat generation during sonication process, the sample's container was placed in an ice-water bath. After sonication, the prepared suspension was transferred to a temperature controlled water bath and the temperature gradually increased from ambient temperature to 80 ± 1 °C. MDI (0.33 g, 1.33 mmol) was added to the above-mentioned mixture under stirring within 15 min and the dispersion was then mechanically stirred at a constant speed of 400 rpm and held at 80 °C for 4 h under nitrogen. The MDI modified silica is shown by M-SiO<sub>2</sub>. In the second stage, to the above mixture, HEMA (0.16 mL) was added and the mixture was thoroughly stirred at 80 °C for 7 h under nitrogen. After cooling to room temperature, the suspension was centrifuged (7000 rpm) and the residue was washed three times with fresh portion of toluene (about 25 mL) and the MDI-HEMA modified silica nanoparticles (MH-SiO<sub>2</sub>) were dried at 60 °C in a low pressure oven until a constant weight was obtained.

### 2.4. Encapsulation of MH-SiO<sub>2</sub> nanoparticles via miniemulsion polymerization

The encapsulated modified silica was synthesized through a two-step route, according to the following method:

Dispersion of MH-SiO<sub>2</sub> in monomer nano-droplets: BuA (5.64 g), MMA (6.12 g), MAA (0.24 g), and definite amount of MH-SiO<sub>2</sub>, according to Table 1, were premixed through sonication at 80% amplitude (Bandelin, HD3200) for 5 min. HD (0.5 g) was dissolved in the monomer phase and the obtained mixture was dispersed in a defined amount of distilled water in the presence 0.1 g NaHCO<sub>3</sub> as the buffer, 0.6 g SDS and 0.15 g Triton X-100 as ionic and non-ionic surfactants, respectively. By adjusting the amount of water in this step, the solid content of latexes was kept approximately 20 wt%

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