



Chemical modification of TiO₂ nanoparticles as an effective way for encapsulation in polyacrylic shell via emulsion polymerization



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ABSTRACT

Encapsulation of inorganic nanoparticles by polymers is one of the interesting research topics that lead to the synthesis of nanocomposites. These nanocomposite materials comprise the properties of both organic polymer and inorganic nanoparticles. Here, hybrid latex particles with core-shell nanostructure were prepared via semi-batch emulsion polymerization. Copolymers of (methyl methacrylate-butyl acrylate) and (dimethylaminoethyl methacrylate-butyl acrylate-acrylic acid) were formed as the inner and outer layers, respectively on the surface of modified TiO₂ nanoparticles as the core. In order to create compatibility between inorganic and polymeric phases, modification of TiO₂ nanoparticles was performed with glycidyl methacrylate with an optimized procedure for the first time and then emulsion polymerization was carried out. The products of each step were fully characterized. The results of dynamic light scattering, 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 85 and 120 nm for 0–5 wt% of the modified TiO₂ nanoparticles. Physico-mechanical properties of the obtained nanocomposite films were studied by DMTA. It was found that using only 3 wt% of modified TiO₂ improved those properties of resulting films remarkably.

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1. Introduction

Organic–inorganic hybrid materials have been the subject of extensive studies recently [1–4]. One of the hottest topics in this field is hybrid latexes containing (modified) inorganic nanoparticles and the polymer particles. Inorganic/organic nanocomposite systems, which inorganic particles are incorporated into the polymer matrix, are new class of polymeric materials that combine the properties of both components. In other words, the polymer component with excellent optical property, flexibility and toughness can improve the brittleness of inorganic particles and besides, inorganic particles will increase the strength and modulus of polymers [5–8].

Among inorganic nanoparticles, titanium dioxide (TiO₂) is widely used as a white pigment in ink, coating, paint, rubber, cosmetic, and plastic because of its excellent scattering properties [9]. However, it has the disadvantage of having a very high density, which makes it susceptible to gravitational settling and decrease

in contrast with time [10]. Also agglomeration causes a decrease in the desired optical and physical properties of TiO₂ particles [11]. Because of these drawbacks, coating of TiO₂ particles with a layer of polymeric material (core-shell morphology) would be essential to lower the average density and avoid undesired agglomeration.

By decreasing particles size (especially in nanoscale), their surface free energy increases and the tendency of particles toward agglomeration will be increased [12]. In addition, there is another concern referring to the difference in surface tension between polymeric materials and inorganic particles. Surface modification is the key resolution to improve the interfacial interaction between TiO₂ particles and the polymeric phase and two approaches are usually used for this reason. In the first method, these particles are coated with inorganic materials with higher hydrophilicity (such as SiO₂ and Al₂O₃) with respect to TiO₂ and this will improve water dispersibility of titanium dioxide [13–16]. In the second method, TiO₂ surface becomes more organophile to make it more compatible with the organic polymers. This can be achieved by three procedures: (i) macroinitiators are fixed on the surface of TiO₂ and thus, these particles can act as initiators during polymerization [17]. (ii) TiO₂ particles are first encapsulated by inorganic SiO₂ and/or Al₂O₃ layers and then they are modified by silane coupling agents for graft polymerization [18]. (iii) Using coupling agents, such as silanes or

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fatty acids, which are directly grafted on the bare TiO₂ surfaces through chemical reaction between existing hydroxyl groups on TiO₂ surface and the coupling agents [19–21]. However, physical modification of TiO₂ particles with stearic acid and dodecanol has not shown adequate efficiency according to the slow migration of the modifier into the water phase during encapsulation process [18,19]. On the other hand, application of some sophisticated coupling agents like polybutene–succinimide pentamine has been reported recently [21,22]. To provide a good compatibility, it is beneficial to chemically bond the polymer chains to the particles surface. This can be achieved by the polymerization of a monomer in the presence of TiO₂ particles bearing polymerizable groups or initiator groups on their surfaces.

Heterogeneous polymerization, especially emulsion polymerization, is an effective way of producing nanoparticles with various architectures [23]. Several patents [24,25] and articles deal with the encapsulation of colloidal metals, sol–gel type oxides (SiO₂, TiO₂) and other inorganic materials [5,6,26] to give organic–inorganic hybrid dispersions, where the polymer shell is built in situ by means of conventional emulsion [5], seeded emulsion [27], miniemulsion [28], and related dispersed-phase polymerization processes [29].

The aim of this work is to prepare TiO₂/acrylic copolymer nanocomposite particles with core–shell morphology through emulsion polymerization technique. To make the encapsulation process more efficient, TiO₂ nanoparticles were chemically modified with glycidyl methacrylate, for the first time. This will improve the final properties due to the prevention of migration of TiO₂ nanoparticles from the polymeric phase. The modified TiO₂ nanoparticles were used as the seed particles in emulsion polymerization and the resulting particles were fully characterized to investigate their microstructure properties.

2. Experimental

2.1. Materials

The monomers, dimethylaminoethyl methacrylate (DMAEMA) and methyl methacrylate (MMA) both from Merck Chemical Co., glycidyl methacrylate (GMA) from Aldrich, butyl acrylate (BuA) from Fluka and acrylic acid (AA) from BASF were purchased and used as received. Sodium dodecyl sulfate (SDS) and Triton X-100 from Aldrich, potassium persulphate (KPS), anhydrous aluminum trichloride (AlCl₃) and sodium bicarbonate (NaHCO₃) (analytical grade) from Merck Chemical Co. were used without any further purification. Titanium dioxide (TiO₂) nanoparticles (average particle size) of 45 nm and specific surface area (Brunauer, Emmett and Teller (BET) analysis) of 45 m² g⁻¹ with rutile phase and without any pre-treatment were supplied by Nanoshell. Deionized (DI) water was used in all recipes.

2.2. Characterization

The sonication was performed by a 20 kHz ± 500 Hz ultrasonic generator, SONOPULS Ultrasonic homogenizer, Model HF-GM 2200 (BANDELIN electronic GmbH and Co. KG, Berlin, Germany) and the sonication probe was a titanium microtip (MS-76) with the diameter of 3 mm. 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. Dynamic mechanical thermal analysis (DMTA) was performed using Tritec 2000 DMA (Triton Technology Co. England). 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

Table 1
Samples with different m-TiO₂ content.

Sample	m-TiO ₂ (g)	m-TiO ₂ (wt%)*
C-1	0	0
C-2	0.58	1
C-3	1.16	2
C-4	1.74	3
C-5	3	5

* m-TiO₂ weight percent was measured relative to the polymer content.

(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.

2.3. Preparation of modified TiO₂ nanoparticles (m-TiO₂)

Surface treatment of TiO₂ nanoparticles was conducted in a two-stage process. In the first stage, 1 g TiO₂, 5 mL GMA and 0.2 g AlCl₃ were added to 100 mL of dried THF containing 0.1 g hydroquinone as the radical inhibitor and the mixture was ultrasonically irradiated for 5 min in an ice bath. In the second step, the dispersion was transferred into a flask equipped with a condenser in an oil bath at 65 °C and stirred gently using a magnetic stirrer for 24 h. Finally, it was centrifuged (9000 rpm, 20 min) and the precipitates were washed with THF. The washing procedure was repeated three times and the precipitates were dried at 30 °C for 48 h.

2.4. Seeded emulsion polymerization

Latexes were prepared by seeded semi-continuous emulsion polymerization in a 500 mL four-necked round bottom glass reactor, which was equipped with a reflux condenser, mechanical stirrer, dropping funnel, and nitrogen gas inlet. Table 1 shows different amounts of m-TiO₂ that were used in the latex recipes.

In a typical procedure, m-TiO₂ was dispersed in 100 mL distilled water in the presence 0.19 g NaHCO₃ as the buffer, 0.42 g SDS and 0.105 g Triton X-100 as ionic and non-ionic surfactants respectively, in an ultrasound bath for 2 h. 0.19 g KPS as the initiator was dissolved in a 10 mL of distilled water and added to the above mixture. Then it was transferred into the reactor. The initial charge was stirred at 300 rpm and heated up to 70 °C. In order to form the first polymeric layer, 21.6 g BuA and 25.3 g MMA were premixed and fed into the reactor with a constant flow rate during 120 min. After addition of the monomers, the mixture was stirred for 10 min. Following this stage and in order to prepare the second polymeric layer, 9.75 g BuA, 0.18 g AA and 1.04 g DMAEMA were added in 30 min dropwise. The resulting latex was allowed to stir for 60 min at the end of addition step to reach to conversion of about 97%.

3. Results and discussion

Nowadays it is difficult to ignore the role of inorganic particles in the latex industry due to their remarkable improvement in physical and mechanical properties of the final product. One of the most important inorganic nanoparticles is titanium dioxide that is widely

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