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Miniemulsion polymerized titania/polystyrene core–shell nanocomposite particles based on nanotitania powder: Morphology, composition and suspension rheology

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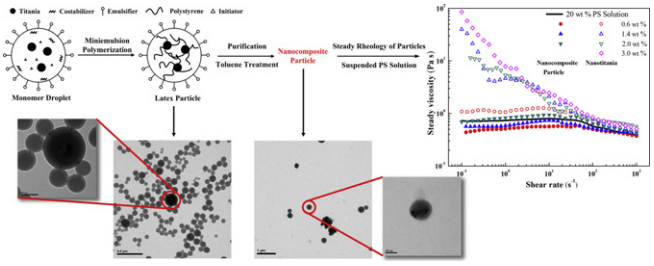
HIGHLIGHTS

- MPS modification improves the dispersibility of nanotitania in organic medium significantly.
- Core–shell nanocomposite particles of controllable size are prepared.
- Nanocomposite particles of 200 nm in diameter contain 22 wt.% cross linked PS shell.
- Nanocomposite particle suspensions deviate from Stokes–Einstein prediction.

GRAPHICAL ABSTRACT



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ABSTRACT

Core–shell nanocomposite particles with a diameter of 200 nm and containing 22 wt.% polystyrene (PS) and 78 wt.% titania were fabricated via miniemulsion polymerization of styrene in the presence of modified nanotitania powder. The PS shell of nanocomposite particles had a crosslinked structure. The effects of reaction temperature, emulsifier concentration, and costabilizer on morphology, size and size distribution were investigated. By adjusting these parameters, it was able to control the size and morphology of the nanocomposite particles. The nanocomposite particles had a fine dispersibility and compatibility with PS solution. Steady rheology of the core–shell nanocomposite particles suspended PS solution revealed a slight viscosity reduction deviating from Stokes–Einstein prediction at 0.6 wt.% particle loading and a slight viscosity increase to the level of pure PS solution at 2.0 wt.% particle loading, which was significantly different from the nanotitania suspensions.

1. Introduction

The design and fabrication of inorganic-polymer core–shell nanocomposite particles have gathered considerable interests recently, since these particles provide a new approach to construct functional nanostructured materials [1–3]. Inorganic-polymer core–shell structure combines the properties of the rigid core and the flexible shell ideally. The polymer shell provides the particles a fine compatibility with polymeric materials and also prevents the agglomeration of particles. Moreover, by adjusting the chemical composition of core–shell nanocomposite particles, for instance, titania is employed, they show some special properties in optics [4], electronics [5], and photocatalysis [6] and hence are potentially useful in the areas of coatings, cosmetics, catalysts and solar cells [7].

Varieties of encapsulation techniques have been developed to fabricate core–shell nanocomposite particles including emulsion polymerization [8,9], dispersion polymerization [10,11], miniemulsion polymerization [12–14], surface initiated controlled/living radical polymerization [15,16] and so on. Among these methods, the use of miniemulsion polymerization has been critical to fabricate core–shell nanocomposite particles with regular morphology

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Table 1
Recipes used for miniemulsion polymerizations of styrene in the presence of MPS-modified nanotitania.

Runs	Modified nanotitania (wt.%)[a]	AIBN (wt.%)[a]	HD (wt.%)[a]	SDS (mM)[b]	OP-10 (g)	$NaHCO_3$ (mM)[b]	Temperature (°C)
1	10	1	5	24	0.2	10	70
2	10	1	5	24	0.2	10	80
3	10	1	5	8	0.2	10	70
4	10	1	5	16	0.2	10	70
5	10	1	5	24	0.2	10	70
6	10	1	5	32	0.2	10	70
7	10	1	5	40	0.2	10	70
8	10	1	0	8	0.2	10	70
9	10	1	7	8	0.2	10	70
10[c]	0	1	5	8	0.2	10	70

[a] Base on monomer.
[b] Base on aqueous.
[c] Pure PS sample synthesized for reference.

and homogeneous size distribution. In miniemulsion polymerization, the monomer droplets containing inorganic particles act as nanoreactors and polymerize via droplet nucleation in situ [17].

However, miniemulsion polymerization system containing inorganic particles is quite complex. Factors such as homogenous energy, temperature and emulsifier concentration greatly influence on the morphology, size distribution and encapsulation efficiency of the nanocomposite particles. Most of the works have been synthesized from inorganic particles made by sol–gel methods. There are few papers employing industrial nanopowder as raw-material which is more practical.

In this article, nanotitania powder is employed to synthesize nanocomposite particles with polystyrene (PS) as the shell layer. The effects of reaction temperature, emulsifier concentration, costabilizer were studied. The structure and chemical composition of nanocomposite particles were carefully characterized. Steady rheological study was used to investigate the dispersion and properties of nanocomposite particles suspended in PS solution.

2. Materials and methods

2.1. Materials

Styrene (Hangzhou Chem. Reagent, China) was distilled under reduced pressure and stored at −30 °C before use. γ-Methacryloxypropyl trimethoxysilane (MPS), hydrophilic nanotitania powder with a diameter of 25 nm, 2,2′-azobisisobutyronitrile (AIBN), hexadecane (HD) and Aliquat 336 (Aladdin Reagent) were of analytical grade and were used as received. Polyoxyethylene nonylphenyl ether (OP-10), sodium dodecyl sulfate (SDS), sodium bicarbonate ($NaHCO_3$), hydrofluoric acid (HF), ethanol and toluene of analytical purity were provided by Sinopharm Chem. Reagent, China. Deionized water was used throughout the work.

2.2. Synthesis of MPS-modified nanotitania

Nanotitania powder was treated at 400 °C for 4 h. The powder and a certain amount of MPS were mixed with 100 mL toluene by magnetic stirring. The mixture was ultrasonicated for 10 min (output power 600 W, work time 5 s, pause time 5 s) and was poured into 250 mL three-necked glass reactor equipped with condenser and mechanical stirrer in an oil bath. The reaction was carried out for 6 h at 100 °C. The MPS-modified nanotitania was obtained by centrifugation (at 6000 rpm for 10 min) and redispersion in ethanol for 4 times. The deposit was dried to constant weight at 70 °C in vacuum for 24 h.

2.3. Synthesis of titania/PS core–shell nanocomposite particles

All the components required in this procedure were divided into two parts. One was aqueous phase, which included 100 mL deionized water, OP-10, $NaHCO_3$ and SDS. The other was oil phase, which composed of 10 mL styrene, modified nanotitania, HD and AIBN. All the recipes were listed in Table 1. The oil phase without AIBN was mixed for 10 min by stirring and was ultrasonicated in an ice bath for 10 min (output power 500 W, work time 3 s, pause time 7 s) to obtain a homogenous dispersion. Then AIBN was dissolved in the oil phase. The oil phase was added to the aqueous phase and the O/W mixture was mixed for 30 min by magnetic stirring for pre-emulsification. The O/W mixture was ultrasonicated in an ice bath for 10 min under the same condition. The miniemulsion was then stirred for 30 min, in order to redistribute the system in a more homogenized state [18]. The miniemulsion was poured into 250 mL three-necked glass reactor equipped with condenser and mechanical stirrer in an oil bath. The reaction was carried out at 70 °C for 2 h under stirring rate 200 rpm. After polymerization, the product was demulsificated and purified from emulsifier by centrifugation (at 3000 rpm for 10 min) and redispersion in 60 °C deionized water for 4 times. The acquired product included PS particles and nanocomposite particles. Toluene was used to dissolve the PS particles. Undissolved nanocomposite particles were collected by centrifugation. Finally, the obtained nanocomposite particles were dried at 70 °C in vacuum for 24 h.

2.4. General procedure for cleavage of PS from nanocomposite particles

Nanocomposite particles (100.0 mg) were suspended in 2 mL toluene, along with 10.0 mg phase transfer catalyst Aliquat 336. Then 2 mL 40% HF solution was added [19], and the reaction was performed under stirring at 80 °C until the white opaque mixture became clear. The toluene phase was taken out and was added dropwisely into ethanol to precipitate PS. After that, PS was recovered by centrifugation and dried at 50 °C, yielding white powders.

2.5. Steady rheological study of particles suspended PS solution

All the materials were dried before use. A certain amount of nanotitania powder or nanocomposite particles was suspended in 20 wt.% PS-toluene solution by stirring and ultrasonication. Suspensions were stirred over night to obtain a homogenous dispersion. Steady rheology was performed on AR-G2 (TA, USA) under shear rate from 0.1 s^{-1} to 1000 s^{-1} with parallel plate grippers of 25 mm in diameter at 25 °C. All the recipes of the suspensions investigated were listed in Table 2.