Advanced Powder Technology 20 (2009) 361–365

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Paper

Importance of dispersibility of TiO_2 in preparation of TiO_2-dispersed microspheres by Shirasu porous glass (SPG) membrane emulsification

M. Takeda [a,*], E. Tanabe [a], T. Iwaki [b], A. Yabuki [b], K. Okuyama [b]

[a] Hiroshima Prefectural Institute of Industrial Science and Technology, 3-10-32, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-0046, Japan
[b] Chemistry and Chemical Engineering, Graduate School of Engineering, Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

ARTICLE INFO

Article history:
Received 11 September 2008
Received in revised form 26 January 2009
Accepted 2 February 2009

Keywords:
Titanium oxide
SPG emulsification
Microsphere
Bead mill dispersion
Ultrasonic dispersion

ABSTRACT

The preparation of the highly refractive transparent TiO_2-dispersed microspheres with uniform size was studied. These nanocomposite microspheres were prepared via TiO_2 dispersion in an acrylic monomer and the emulsification by the Shirasu porous glass (SPG) membrane technique. Two kinds of the dispersion methods (bead mill dispersion with fine beads and ultrasonic dispersion) were carried out. The suspension prepared by bead mill included well-dispersed TiO_2 nanoparticles and led to the uniformly sized TiO_2-dispersed microspheres. It was indicated that the dispersibility of TiO_2 in a monomer was the important factor in this process.

1. Introduction

Composite polymer materials incorporating inorganic particles have been studied in the fields of pharmacy, catalysts, electronics, optics, etc. The incorporated inorganic particles render the polymer materials functional. It is further effective to use nanoparticles for preparing highly functional polymer materials because of their nano-size effect. In the field of optics, nanocomposite materials including highly refractive nanoparticles such as TiO_2 can be used to manufacture light diffusion films [1]. These microspheres are required to be transparent and have a uniform particle size.

Several methods are used for the preparation of uniformly sized microspheres. Taguchi et al. reported that the uniformity of microspheres can be improved by controlling the viscosity of composite monomers and the rotational frequency during suspension polymerization [2]. However, this procedure is complicated. It is possible to obtain monodispersed microspheres (with a coefficient of variation less than 5%) by spontaneous sedimentation; however, it is very time-consuming, for example, it takes several months. In order to successfully prepare monodispersed microspheres, the Shirasu porous glass (SPG) membrane emulsification technique has been advantageous in terms of ease of operation and short operation period. In this procedure, an oil phase such as an organic solvent or a monomer is forced to permeate through SPG membrane pores into an aqueous phase to obtain uniformly sized oil droplets. Even in this method, the existence of nanoparticles in the oil phase makes it difficult to prepare uniformly sized oil droplets. It is because the oil phase can wet the SPG membrane easily due to the hydrophilicity of the dispersant present in the oil phase. To avoid wetting, Supsakulchai et al. added hydrophobic additives such as methyl laurate, hexadecane, and hexadecanol to the oil phase (a polymer dissolved in an organic solvent) [3–5]. However, it was observed during these studies that TiO_2 sometimes plugged the pores of the SPG membrane because it was poorly dispersed in the oil phase. To overcome this problem, it is necessary to disperse TiO_2 on a nano scale in the oil phase. Furthermore, it is favorable to disperse TiO_2 in a monomer instead of a polymer/organic solvent, as reported by Supsakulchai et al. More number of monomers, as compared to polymers/organic solvents, can be used to prepare composite suspensions.

It is extremely difficult to disperse nanoparticles in a solution due to the tendency of the particles to agglomerate, as per the stabilization energy theory. Inkyo et al. achieved the dispersion of TiO_2 in water up to a primary diameter by using a bead mill [6,7]. In our previous studies, TiO_2 was dispersed almost up to the primary diameter in an acrylic monomer [8]. These TiO_2-dispersed solutions are highly transparent and are suitable for manufacturing optical materials wherein optical transparency is necessary. It can be expected that the plugging of the SPG membrane due to TiO_2 can also be prevented.

In this study, a 1 wt.% TiO_2-dispersed monomer was prepared by the bead mill dispersion method, and the TiO_2-dispersed monomer was emulsified into an aqueous phase without causing

* Corresponding author. Tel.: +81 82 431 0200; fax: +81 82 431 0201.
E-mail address: takeda@sankaken.gr.jp (M. Takeda).

0921-8831/$ - see front matter © 2009 The Society of Powder Technology Japan. Published by Elsevier BV and The Society of Powder Technology Japan. All rights reserved.
doi:10.1016/j.apt.2009.02.009

plugging of the membrane. It was confirmed by TEM that TiO_2 was well-dispersed in the nanocomposite microspheres.

2. Experimental

2.1. Materials

TiO_2 nanoparticles (MT150W, Tayca) with a primary diameter of 15 nm and a needle-like rutile crystal structure were used for dispersion. Neopentyl glycol dimethacrylate (Hitachi Chemical) and Solsperse (Lubrizol Japan Ltd.) were used as a monomer (dispersion medium) and a dispersant, respectively.

5 wt.% polyvinyl alcohol (PVA) and sodium dodecyl sulfate (SDS) were added in the aqueous phase for SPG emulsification. Hexadecanol was added in the oil phase as a hydrophobic additive. Benzoyl peroxide (BPO), known for its high reactivity, was used as a polymerization initiator.

All the chemicals were used as received.

2.2. TiO_2 dispersion

TiO_2 (1 wt.%, based on the total amount of suspension) was dispersed by two different methods (ultrasonic dispersion and bead mill dispersion).

For bead mill dispersion, a bead mill (Kotobuki Industries Co., Ltd.) filled with fine zirconia beads (50 μm diameter) was used. TiO_2 (3.0 g), the dispersant (2.4 g), and the monomer (294.6 g) were pumped into the bead mill at a flowrate of 4 ml/s. The peripheral speed of the rotor in the centrifugation section was set at 12 m/s. For ultrasonic dispersion, TiO_2 (2.0 g) was dispersed in the monomer (196.4 g) solution including the dispersant (1.6 g) by using an ultrasonic cleaning machine (VS-150, As One Corporation). The amounts of TiO_2 and dispersant based on the total amount were the same in both the dispersion methods.

The dispersibility and particle size distribution of TiO_2 in the suspension were determined by using a particle analyzer (FPAR-1000, Otsuka Electronics Co., Ltd.) on the basis of the dynamic light scattering theory and a cumulant method.

The turbidity (NTU) of the suspensions was measured by using a turbidity meter (HI-93703, Hanna Instruments Ltd.) after diluting them with a pure monomer.

2.3. SPG membrane emulsification

A schema of the SPG membrane emulsification apparatus is shown in Fig. 1. An o/w system consisting of an oil phase and an aqueous phase was used. The oil phase, consisting of the TiO_2-dispersed monomer (70 g), hexadecanol (4.0 g), and BPO (0.7 g), was forced to permeate through the SPG membrane pores (pore diameter: 2.0 μm) into the aqueous phase, consisting of a 5 wt.% PVA aqueous solution (150 g) and SDS (0.3 g). The aqueous phase was rotated by using a centrifugal pump. The pressure for permeation was gradually applied by using a precise pressure regulator. The pressure applied at the initiation of emulsification was defined as the critical pressure. The emulsification temperature was held constant at 30 ± 1 °C.

The emulsified droplets were observed by using an optical microscope.

2.4. Evaluation of TiO_2-dispersed microspheres

The droplets, prepared as described in the previous section, were polymerized under an N_2 atmosphere at 80 °C for more than 16 h to obtain microspheres.

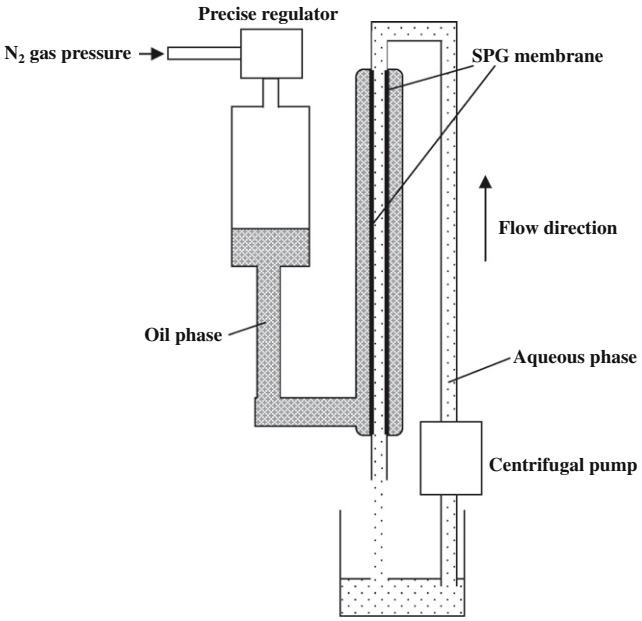

Fig. 1. Schema of the SPG membrane emulsification apparatus.

The morphology of the microspheres was observed by using a scanning electron microscope (SEM) (JSM-6340F, JEOL Ltd.) and a transmission electron microscope (TEM) (JEM-3000F, 297 kV, JEOL Ltd.). In order to observe a cross-sectional view of the microspheres, a focused ion beam (FIB) (FB-2000A, Hitachi Ltd.) was used.

TiO_2 concentration was measured by using a differential thermal analyzer (TG8120, Rigaku) by varying the temperature from room temperature to 1000 °C at a rate of 20 °C /min under an O_2 atmosphere (flowrate of 50 ml/min). The TiO_2 concentration was estimated from the residual weight.

The particle size distribution of the microspheres was measured by using an electronic particle counter (Coulter Multisizer 3, Beckman Coulter Inc.).

3. Results and discussion

3.1. TiO_2 dispersion

The time dependence of the dispersed diameter and the particle size distribution of TiO_2 are shown in Figs. 2 and 3, respectively. When bead mill dispersion was carried out for 440 min, the dispersed diameter of TiO_2 reduced and then reached the smallest value (47.6 nm). Following that, it increased as a result of reagglomeration [6]. The dispersed diameter was less than 100 nm when bead mil dispersion was carried out for 20 min. TiO_2 was better dispersed by this method than the ultrasonic dispersion method, as described in the next paragraph.

During 120 min of ultrasonic dispersion, the dispersed diameter of TiO_2 reduced and then remained almost constant (ca. 190 nm). The particle size of TiO_2 dispersed by ultrasonic dispersion was more widely distributed as compared to that of TiO_2 dispersed by bead mill dispersion. Therefore, TiO_2 was not monodispersed by ultrasonic dispersion. The TiO_2-dispersed monomers are shown in Fig. 4; the suspension dispersed by the bead mill method was considerably transparent (turbidity: 906 NTU), while that dispersed by the ultrasonic dispersion method was opaque (turbidity: 15,200 NTU). TEM images of the TiO_2-dispersed monomers are shown in Fig. 5. TiO_2 was dispersed almost up to the primary diameter by the bead mill dispersion method. However, a large aggre-