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ORIGINAL CONTRIBUTION

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Titanium dioxide/poly(methyl methacrylate) composite microspheres prepared by in situ suspension polymerization and their ability to protect against UV rays

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Abstract Homogenously dispersed TiO_2/poly(methyl methacrylate) (PMMA) composite microspheres were produced in the size range of 1–10μm and the interfacial characteristics of TiO_2 and PMMA in suspension polymerization were considered. In electron microscopy observation, it was found that TiO_2 nanoparticles were embedded homogeneously in the PMMA phase. This study elucidates that the interfacial compatibility between TiO_2 and PMMA played a decisive role in producing the composite microspheres structured with inner TiO_2 and continuous PMMA, which was achieved by treating the surface of the TiO_2 particles hydrophobically. The TiO_2/PMMA composite microspheres produced showed good ability to protect against UV rays and are therefore of great usefulness in cosmetic formulations.

Keywords Microspheres · In situ suspension polymerization · Interfacial compatibility · UV rays

Introduction

Inorganic/polymer composite microspheres with diameters of 1–10 μm have received some interest in electronics, cosmetic, and pharmaceutical industries, agriculture, and in toner and paint production owing to their mechanical and functional properties [1, 2, 3]. Encapsulation of inorganic materials in a polymer shell provides better mechanical properties, such as film strength, appearance, and durability [5, 6, 7, 8, 9]. Most of all, the improvement in dispersion stability is one of the most significant characteristics of inorganic/polymer composite microspheres.

In producing inorganic/polymer composite microspheres, usually, the dispersion stability of the inorganic particles must be improved substantially in the organic medium. A number of studies indicated that inorganic particles could be dispersed stably by adsorbing effective macromolecular surfactants or stabilizers [10, 11, 12]. Recently, the accommodation of inorganic nanoparticles in miniemulsion droplets was introduced using a system where there was strong interaction between stabilizer and emulsion droplets, and consequently submicron-sized inorganic/polymer particles were obtained [13]. However, the successful loading of inorganic particles within micron-sized polymer particles was not reported, even though they could find many industrial applications.

In the present contribution, we synthesized TiO_2/poly(methyl methacrylate) (PMMA) microspheres by in situ suspension polymerization. The dispersion stability of TiO_2 in monomer mixtures is largely dependent on the surface characteristics of TiO_2 in the dispersed state and during polymerization. In this study, the morphological study of TiO_2/PMMA composite microspheres was carried out by considering the surface characteristics of TiO_2 particles. Moreover, their ability to protect against UV rays is estimated for a simple cosmetic formulation.

Experimental

Materials

Methyl methacrylate (MMA, 99% assay), 2,2′-azobis-2,4-(dimethyl valeronitrile) (ADVN), and ethylene glycol dimethyl methacrylate (EGDMA) were purchased from Junsei Chemical Co. Poly(vinyl alcohol) (PVA 217, 87–89% saponification) was kindly supplied by Kururay Chemical. Co. TiO_2 nanoparticles SA-TTO-S-4 were donated by Miyoshi Kasei. The particles are 15–30 nm-sized TiO_2 coated with 6–8% stearic acid and 10 wt% oligomeric dimethyl silicone. The TiO_2 used in this study is an anatase phase-rich crystal. TiO_2 particles MT-100T coated with only stearic acid were also purchased from Ikeda Co. and the effect of surface characteristics on the dispersion stability was compared with that of SA-TTO-S-4.

In situ suspension polymerization

TiO_2/PMMA composite microspheres were produced by in situ suspension polymerization. Dimethyl silicone treated or untreated TiO_2 nanoparticles were redispersed in the mixture of MMA, EGDMA, and ADVN by sonification for 5 min at room temperature. Then, the TiO_2 dispersion in the mixed monomer solution was poured into 2 wt% PVA aqueous solution and emulsified with a homogenizer at 5,000 rpm for 5 min. Polymerization was then carried out under mild stirring in a double-walled glass reactor equipped with a stirrer, a reflux condenser, thermocouples, and a nitrogen gas inlet system. The particles produced were washed repeatedly by decantation in water and ethanol and dried under vacuum at ambient temperature. The composition and designation of each sample are listed in Table 1. Here, TiO_2/PMMA composite microspheres are symbolized by TP-α, where α means the concentration of TiO_2 nanoparticles in the PMMA phase.

Determination of in vitro sun protection factors

To estimate the ability of composite microspheres to protect against UV rays, simple water-in-oil (W/O) emulsions were prepared by adding slowly 70 wt% distilled deionized (DDI) water into the clyclic dimethyl polysiloxane continuous phase containing the composite microspheres and 2 wt% polyethylene glycol (30) dipolyhydroxystearate (Uniquema Americas) at 75 ± 5 °C while homogenizing at 7,000 rpm. Then, a sample (2 $\mathrm{mgcm^{-2}}$) was placed onto Transpore tape (3M). After 15 min, the sun protection factor (SPF) was measured five times with a SPF analyzer system (Optometrics, USA). The SPF was calculated from the monochromatic protection factor (MPF) as described by Diffey and Robson [14]:

$$\mathrm{SPF} = \frac{\sum_{290}^{400} E_\lambda B_\lambda}{\sum_{290}^{400} \frac{E_\lambda B_\lambda}{\mathrm{MPF}_\lambda}},$$

where E_λ is the spectral irradiance of terrestrial sunlight under defined conditions, B_λ is the refractive effectiveness of UV radiation at a specific wavelength in producing delayed erythema in human skin, and MPF_λ is the mean MPF.

Characterization

The apparent sedimentation stability, S_{app}, was assessed by measuring the sedimentation speed of the TiO_2 particles in the monomer mixture. - Monomer dispersions containing 10 wt% TiO_2 nanoparticles were placed in a glass tube of 0.5 cm inner diameter and 20 cm length. Then, the sedimentation stability of TiO_2 was monitored at a given aging time as follows [15]:

$$S_{\mathrm{app}}(\%) = \frac{l(t)}{l_0} \times 100,$$

where, l_0 is the length of the initial opaque dispersion and $l(t)$ is the length of the sediment part at a given time, t, in the tube, respectively.

The images of the microspheres produced were obtained with an optical microscope (OM, Nikon microphot FXA). The surface image was observed with field-emission scanning electron microscope (SEM, Hitachi S-4300). Ultrathin cross sections of the composite microspheres prepared by microtoming the cured epoxy samples were observed with a transmission electron microscope (TEM, JEOL 2010).

Results and discussion

Conventional inorganic nanoparticles have high surface polarity; therefore, when dispersed in an organic medium, they display extremely low stability. It was attempted to overcome the low dispersion stability of the inorganic nanoparticles by treating the surface with organic compounds; however, the organic treatment did not improve the low dispersion stability of the inorganic

Table 1 Composition of monomer mixtures in TiO_2/poly(methyl methacrylate) composite particles (75 ± 5 °C; 3 rpm; 6 h)

Symbol	TiO_2 (g)	Monomer composition				TiO_2 loading efficiency (% w/w)
		Methyl methacrylate (g)	Ethylene glycol dimethyl methacrylate (g)	2,2′-Azobis-2, 4-(dimethyl valeronitrile) (mg)[a]	*n*-Heptane (g)[b]	
TP-0	–	85.00	15.00	100	–	–
TP-10	10	76.50	13.50	90	–	95.5
TP-10N[c]	10	76.50	13.50	90	–	21.6
TP-30	30	59.50	10.50	70	–	90.8
TP-50	35	29.75	5.25	35	35	90.2

[a] 1 wt% concentration based on total monomer weight

[b] Inert diluent, *n*-heptane was used to control the volume fraction of TiO_2 against poly(methyl methacrylate)

[c] Composite particles produced using untreated TiO_2 (MT-100T). In the other cases, SA-TTO-S-4 was used

particles in the organic medium. Here, we propose another route to improve the dispersion stability of inorganic materials, i.e., to produce inorganic/polymer composite microspheres by in situ suspension polymerization.

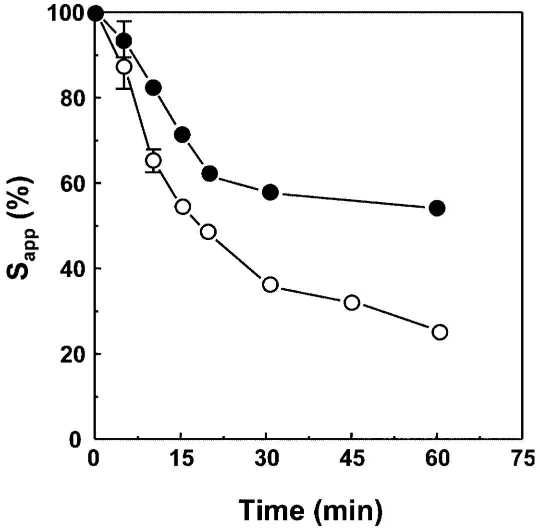

Fig. 1 Apparent sedimentation stability, S_{app}, of TiO_2 nanoparticles in a monomer mixture, methyl methacrylate (*MMA*)/ethylene glycol dimethyl methacrylate (*EGDMA*) = 85/15 w/w. The concentration of the TiO_2 nanoparticles was 10 wt% against the total monomer weights; untreated (*open circles*), treated (*filled circles*)

In order to carry out successfully in situ suspension polymerization, the TiO_2 nanoparticles should have sufficient stability in the monomer droplets during the polymerization. Preliminarily, therefore, interfacial compatibility is required between the TiO_2 particles and the monomer mixture. The sedimentation stability of the TiO_2 nanoparticles in the monomer mixture is shown in Fig. 1. Conventional inorganic particles have a tendency to separate easily in solvents because of their high density and low compatibility with organic materials. In contrast, the dimethyl silicone treated TiO_2 nanoparti-

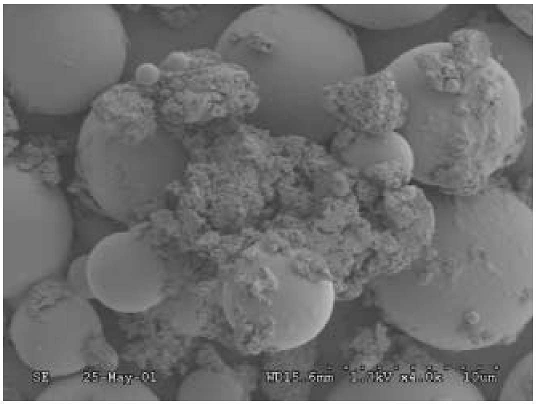

Fig. 2 Scanning electron microscope (*SEM*) photograph of TiO_2/poly(MMA) (*PMMA*) composite microspheres (TP-10N) with untreated TiO_2 nanoparticles (MT-100T)

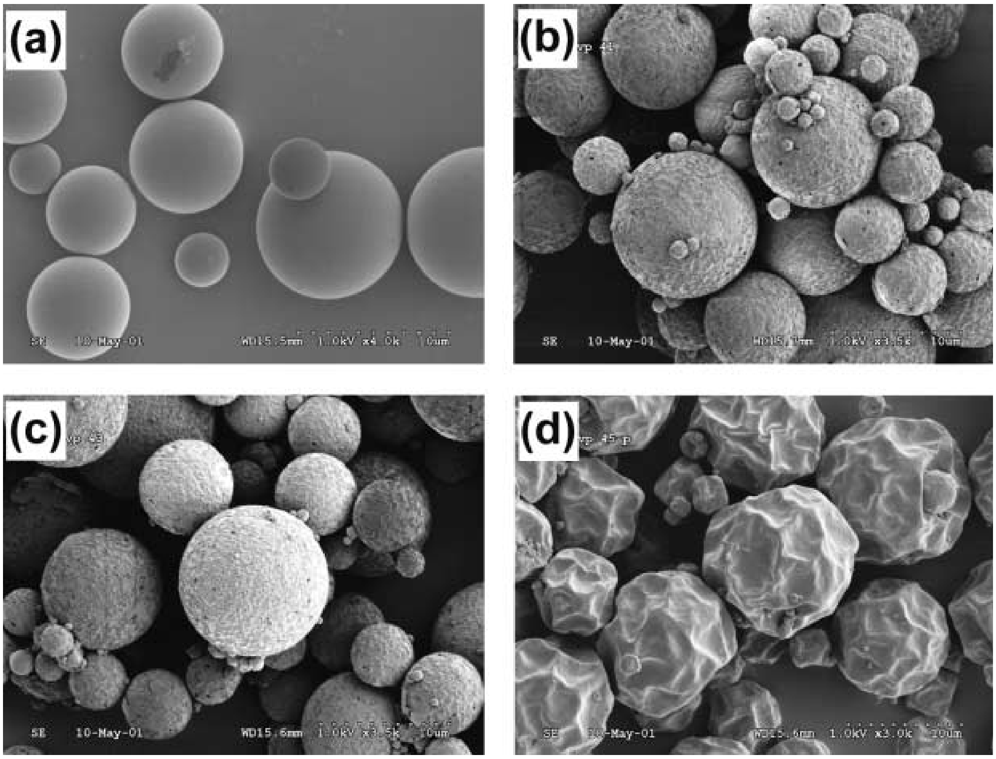

Fig. 3 SEM photographs of TiO_2/PMMA composite microspheres with different concentrations of TiO_2 nanoparticles (SA-TTO-S-4): **a** 0 wt%; **b** 10 wt%; **c** 30 wt%; **d** 50 wt%

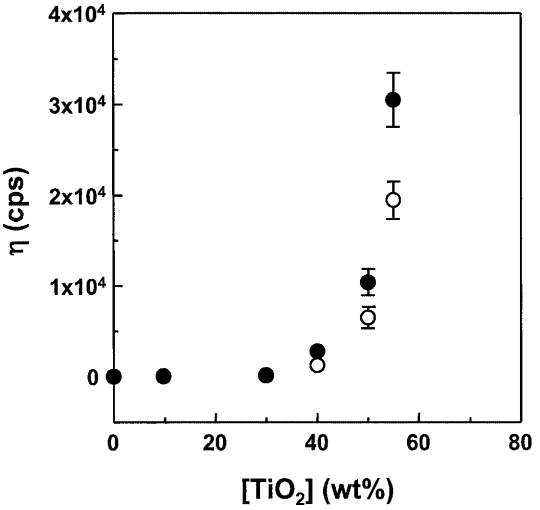

Fig. 4 Variation of the viscosity of TiO_2/MMA/EGDMA mixtures with the concentration of TiO_2. MMA/EGDMA = 85/15 w/w; untreated (*open circles*), treated (*filled circles*)

cles retained their stability for a relatively long time, indicating good compatibility between TiO_2 and the monomer phase [15]. Moreover, it is assumed that the effective conformation of dimethyl silicone chains enhanced the dispersion stability by anchoring on the surface of the TiO_2 particles. Therefore, when polymerized with untreated TiO_2 particles, the elution of a large number of TiO_2 particles from the initial state of droplet formation could be readily observed. As shown in Fig. 2, a large number of TiO_2 agglomerates coexisted with pure PMMA microspheres. Differing from the case of using the untreated TiO_2 nanoparticles, the dimethyl silicone treated TiO_2 nanoparticles were embedded well in the PMMA phase. SEM photographs of TiO_2/PMMA composite microspheres for different concentrations of TiO_2 in the PMMA are shown in Fig. 3. In all the spheres, there was not any aggregation of TiO_2 particles. From these results, it is certain that the surface properties of the inorganic nanoparticles had a decisive influence on the effective formation of inorganic/polymer composite microspheres.

To a concentration of 30 wt%, TiO_2 nanoparticles were redispersed directly in the monomer mixture without any gelation; however, above that concentration, the TiO_2/monomer dispersion gelled in the form of paste. The viscosity change of the TiO_2/monomer dispersions is shown in Fig. 4. A sharp increase in viscosity could be observed at high concentrations of TiO_2 in the monomer mixtures. Because the suspension polymerization cannot be carried out under that condition, the monomer mixture was diluted with an inert solvent, *n*-heptane, and polymerized. Using this approach, TiO_2 nanoparticles could be incorporated homogeneously into the PMMA to about 50 wt% concentration; however, after elimination of *n*-heptane, deformation of the spheres was observed, as shown in Fig. 3d. It was apparent that the elimination of a relatively large volume of *n*-heptane caused the spherical shape of the PMMA composite microspheres to collapse.

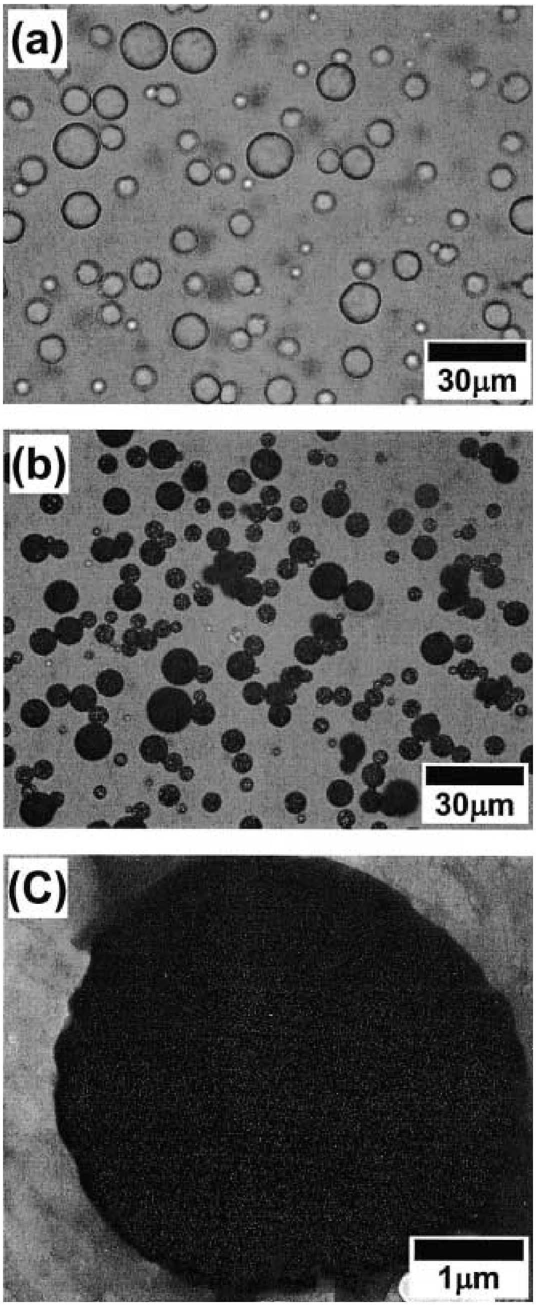

Fig. 5 Optical microscope and transmission electron microscope (*TEM*) images of TiO_2/PMMA composite microspheres: **a** pure PMMA; **b**, **c** TiO_2/PMMA microspheres (TP-30); The TEM image **c** is a thin section of a composite microsphere

The morphology of the TiO_2/PMMA composite microspheres was observed with an OM and a TEM and

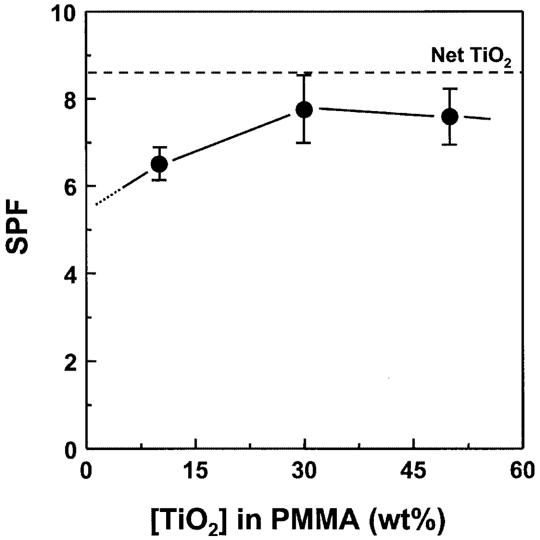

Fig. 6 Sun protection factor (*SPF*) indexes of TiO_2/PMMA composite microspheres in water-in-oil emulsions. The concentration of TiO_2 was changed for a constant concentration of composite microspheres. The net TiO_2 concentration was 3 wt% in the water-in-oil emulsions

is shown in Fig. 5. Pure PMMA microspheres displayed a bright inner phase in an organic medium because of their high refractive index ($n = 1.4893$) (Fig. 5a). However, upon embedding the TiO_2 particles in PMMA, the microspheres showed a dark inner phase (Fig. 5b). This happens because the TiO_2 particles in the PMMA microspheres scattered the light through the polymer phase. The dispersion morphology of the TiO_2 nanoparticles in the PMMA phase was observed with a TEM and is shown in Fig. 5c. The image of an ultrathin cross section of TiO_2/PMMA composite microspheres clearly proved that the TiO_2 particles were embedded well in the PMMA phase.

The ability of TiO_2/PMMA composite microspheres to scatter UV rays was observed in simple W/O emulsions and is shown in Fig. 6. Compared with the net TiO_2 composition, all the composite microsphere compositions displayed slightly low SPFs. This happens because the distribution of the TiO_2 particles had the form of the secondary aggregation on the thin W/O emulsion film, resulting in a comparatively larger free space where the UV rays penetrate. However, because the decrease in the SPF values was negligibly small, it was believed that the TiO_2/PMMA composite microspheres would not cause any problem in the ultimate usage.

From these results it was concluded that in producing inorganic/polymer composite microspheres, one should consider the interfacial compatibility between inorganic and polymer materials. For this purpose, the surface of inorganic nanoparticles must be treated sufficiently with hydrophobic organic materials. In further applications, they are expected to find great usefulness in protecting against strong light and in improving the dispersion stability of inorganic formulations.

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