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Journal of Colloid and Interface Science 310 (2007) 617–623
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

Rheology and UV-protecting properties of complex suspensions of titanium dioxides and zinc oxides

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Received 2 November 2006; accepted 2 February 2007

Available online 12 February 2007

Abstract

Ultra-fine particles of titanium dioxide (TiO_2) and zinc oxides (ZnO) are very attractive as UV-protecting ingredients in cosmetic products. The UV-scattering behavior of complex suspensions in a silicone oil is studied in relation to rheological properties. To control the dispersion stability of suspensions, three polyoxyethylene (POE)-modified silicones of branch-type, $(AB)_n$-type, and ABA-type are used as dispersants. Irrespective of molecular structure, the dispersants can stabilize the TiO_2 and ZnO particles and the flow of both single suspensions is Newtonian with low viscosity. However, the Newtonian flow profiles and high dispersion states are maintained only for complex suspensions prepared with ABA-type dispersant. Since the POE groups which are incorporated between terminal silicones groups attach to the particle surfaces, the steric stabilization is responsible for low viscosity and high dispersions. Because the UV scattering of suspensions is determined by the sizes of flocculated structures, the high transmittance in the visible ranges and low transmittance in the UVA and UVB ranges can be achieved in the presence of ABA-type dispersant.

Keywords: Polyoxyethylene-modified silicones; Suspension rheology; Titanium dioxide; UV-protecting ability; Zinc oxide

1. Introduction

In recent years, knowledge about the effects of ultraviolet radiation (UV) on the skin and health of humans has increased to a great extent. Excessive exposure to UV from the sun causes sunburn, stain, and an increased risk for skin cancers [1,2], when the natural protection mechanisms such as melanin synthesis are overstressed. It is well known that these effects are mainly attributed to the UV in the wavelength range of 280–320 nm, which is referred to as UVB. But the UVA portion with wavelengths of 320–400 is also an important factor [3,4], because it contributes to the induction of erythema. From an application-oriented point, the sun protection factor (SPF) which gives a measure of UV absorption ability of commercial sunscreen products span a broad range and the measuring methods are extensively discussed for establishment of standard evaluation [5].

In cosmetic industries, the interests have been paid to protection of UVB and ultra-fine titanium dioxide (TiO_2) is widely used as an effective UVB-protecting material in sunscreen formulations [6,7]. Compared with other organic UV-absorbents including *p*-amino benzoic acid and octyl salicylate, the ultra-fine TiO_2 particles have advantages of high safety and stability. However, to prevent premature aging of skin, the UVA protection must be ensured in the development of cosmetic sunscreens. Currently, the most widely used inorganic UVA absorber is zinc oxide (ZnO) [8–10]. Therefore, the mixtures of TiO_2 and ZnO particles are expected to give rise to the effective absorption in both UVA and UVB regions by a combination effect.

The UV-protecting cosmetics are generally provided in the form of colloidal suspensions. In ordinary conditions the fine particles such as TiO_2 [11–13] and ZnO [14] dispersed in a liquid tend to form flocs due to interparticle attraction. Since the UV protection is accomplished by light scattering, which de-

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doi:10.1016/j.jcis.2007.02.012

pends chiefly on the refractive index and diameter of particles, the formation of flocculated structures of particles results in a decrease of UV scattering or the hiding power. In manufacturing processes the selection of dispersion method is directly connected with the improvement of UV-protecting ability. Moreover, the final commercial products are strongly required to keep the good stability against flocculation and sedimentation for a long period. Therefore, for formulation of UV-protecting cosmetics, it is important to study the flocculation behavior of suspensions consisting of two different particles.

In a previous paper [15], we studied the relation between the rheological properties and UV-protecting ability for suspensions of ultra-fine TiO_2 particles dispersed in a silicone oil as a function of the molecular structures of polyether-modified silicones which were employed as dispersants. Good agreements are established between them, because the viscosity and dynamic viscoelasticity of suspensions can be closely related to the degree of flocculation. The important result is that the adsorbed conformation of dispersant molecules on particle surfaces determines the colloidal stability. The present paper is designed to evaluate the dispersion stability through rheological methods for complex suspensions of TiO_2 and ZnO and to determine the optimum formulation of sunscreen cosmetics with high UV-protecting ability in both UVA and UVB regions. The role of dispersants in heterogeneous flocculation behavior will be discussed in relation to their molecular structures.

2. Materials and methods

2.1. Materials

The suspensions were composed of ultrafine particles, dispersants, and silicone oil. The ultrafine particles were TiO_2 and ZnO. The TiO_2 (rutile) particles (from Tayca Co., Ltd.) had a spindle form with a shorter diameter of about 10 nm and longer diameter of 30–40 nm. The surfaces were treated with aluminum stearate, the content of which was 17% by weight. The density and surface area of surface-treated TiO_2 were $2.7 \times 10^3\ \mathrm{kg\,m^{-3}}$ and $63.5\ \mathrm{m^2\,g^{-1}}$, respectively. The ZnO particles (from Showa Denko K.K.) had a grain form with a diameter of 30–50 nm. The surfaces were treated with anhydrous silicic acid and dimethylpolysiloxane (DMPS), the content of which was 22% by weight. The density and surface area of surface-treated ZnO were $2.8 \times 10^3\ \mathrm{kg\,m^{-3}}$ and $22\ \mathrm{m^2\,g^{-1}}$, respectively. The silicone oil used as the medium was decamethylcyclopentasiloxane (Shin-Etsu Chemical Co., Ltd.), the density of which was $0.958 \times 10^3\ \mathrm{kg\,m^{-3}}$. Because of low molecular weight, the medium was volatile. The dispersants were three kinds of polyoxyethylene(POE)-modified silicones. Their molecular structures are shown in Fig. 1. Dispersant A (Shin-Etsu Chemical Co., Ltd.) was the branched polymer (called branch-type in this work), in which the POE moieties were incorporated as side chains along the backbone. The molecular weight and HLB value were 12,000 and 4, respectively. Dispersant B (Nippon-Unicar Co., Ltd.) was the polymer with linear conformation, in which the DMPS and POE moieties were alternately repeated in one long chain (called $(AB)_n$-type). The

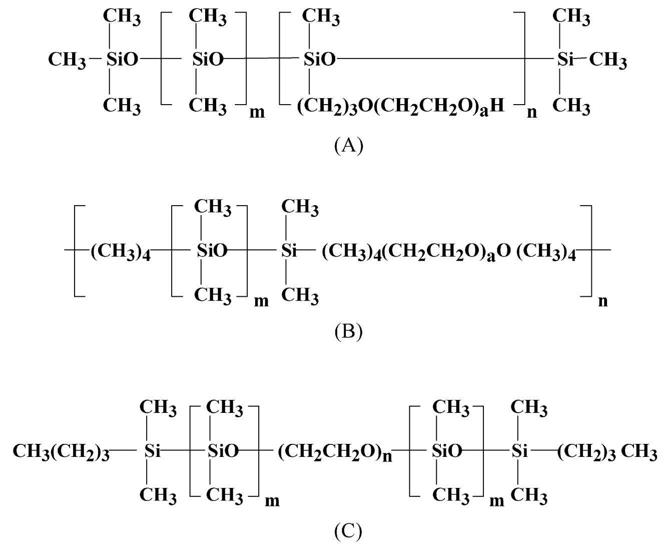

Fig. 1. Molecular structures of polyoxyethylene-modified silicones: (A) branch-type ($a = 8$–10, $m = 30$–60, $n = 2$–5); (B) $(AB)_n$-type ($a = 8$–12, $m = 10$–40, $n = 2$–5); (C) ABA-type ($n = 34$–36, $m = 65$–67).

molecular weight and HLB value were 20,000 and 3, respectively. Dispersant C was the polymer with linear conformation, in which the DMPS moieties were incorporated on the ends of molecule as terminal groups (called ABA-type). The ABA-type dispersant was synthesized for this study from mono-terminal reactive silicone oil (Silaplane from Chisso Co.), PEO and hexamethylene diisocyanate. The molecular weight and HLB value were 11,500 and 2.6, respectively.

The ultra-fine TiO_2 and ZnO particles were dispersed by a paint shaker (Asada Co., Ltd.), in which the glass beads with a diameter of 1 mm were added at a filling factor of 50% by volume. The frequency of vibration was $11\ \mathrm{s^{-1}}$. The dispersion time was 30 min for all suspensions. The particle concentration was 40% by weight. The composition of complex suspensions is expressed as the weight ratio of TiO_2 and ZnO particles. Owing to very close particle densities, the volume concentration of particles was in the range of 18.6–19.0% independent of mixing ratio.

2.2. Methods

Steady-flow and dynamic viscoelastic properties were measured with a cone-and-plate geometry on a rheometer controlled by stress (TA Instruments Co., Ltd. AR-1000N). The cone diameter was 40 mm and the gap angle between the cone and plate was 4°. The shear rates were from 0.01 to $500\ \mathrm{s^{-1}}$ in steady-flow measurements. The dynamic viscoelasticity was measured as a function of frequency at a small stress in the linear regions and as a function of stress at a constant frequency. The angular frequencies were from 0.12 to $62.8\ \mathrm{s^{-1}}$ and the stress amplitude was from 0.1 to 20 Pa. The measuring temperature was 25 °C.

Adsorption of POE-modified silicones on the particle surfaces was measured for 40 wt% suspensions. To determine the concentration of nonadsorbed dispersants, the suspensions were separated by centrifugation at 370,000*g* and the suspension