Dispersion of titanium dioxide nanoparticles in silicone oil using poly(ethylene glycol-b-dimethylsiloxane-b-ethylene glycol) triblock copolymer as dispersants

Presented in The 2nd Progress in Advanced Materials: Micro/Nano Meterials and Applications

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Abstract

Titanium dioxide (TiO_2) nanoparticles are very attractive as a UV protection ingredient in cosmetic, paint and coating industries. However, the preparation of suspension of TiO_2 nanoparticles is rather difficult mainly due to their strong attractive interactions between the very small particles. To overcome this problem, dispersants are usually added to increase distance between the nanoparticles and prevent the agglomeration. The purpose of this study is to find the effective methods for dispersing the agglomerated TiO_2 into nanoparticles. Silicone oil normally used in cosmetic products was used as media. The newly synthesized poly(ethylene glycol-b-dimethylsiloxane-b-ethylene glycol) triblock copolymers were used as non-ionic dispersants. The segment of polyethyleneglycol was expected to anchor on the surface of TiO_2 nanoparticles due to its high polarity while the segment of polydimethylsiloxane had favourable interaction with silicon oil medium. The length of each block was systematically controlled allowing the variation of local interfacial interactions between the TiO_2 nanoparticles and the medium. The efficiency of dispersion was compared by studying properties of the suspension including rheological behavior and UV protection ability.

Keywords: Titanium dioxide, nanoparticle, dispersant, silicone oil

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1. Introduction

Titanium dioxide (TiO_2) is very useful as a UV protection ingredient in cosmetics, paint and coating industries. When mixed with a liquid medium, well-dispersed TiO_2 nanoparticles provides a transparent suspension (Katangur et al., 2006), a property required in UV protection cosmetics and transparent UV protection coatings (Maier and Korting). However, due to small size and high interactive force, TiO_2 nanoparticles tend to agglomerate, which reduces UV protection ability and transparency of the suspension.

To prepare a well-dispersed metal oxide suspension, dispersant is required to increase interparticle distance, reduce agglomeration and stabilize particles in the medium. Polymers dispersants assist in particle dispersion by adsorbing on the particle surface and keep particles apart. Efficiency of the dispersant depends on the equilibrium of particle surface, nature of the medium and dispersant structure.

In this work, poly(ethylene glycol-b-dimethylsiloxane-b-ethylene glycol) triblock copolymers were used as dispersants. The polydimethylsiloxane segments were expected to extend into the silicone oil medium while the polyethyleneglycol segments anchored on the TiO_2 surface. Particle dispersion was studied through rheological behavior and UV protection ability of the suspension. The flocculation mechanisms were discussed in terms of the dispersant molecular structures.

2. Materials and methods

TiO_2 nanoparticles (Merck Co., Ltd.) used in this study were spherical with an average particle size of ~50 nm as shown in TEM micrograph in Figure 1. The silicone oil used as the medium was octamethylcyclotetrasiloxane (Fluka Chemie GmbH CH-9471 Buchs) with the molecular weight of 296 g/mol and viscosity of ~20 cP, measuring at 50 rpm. The non-ionic dispersants were poly(ethylene glycol-b-dimethylsiloxane-b-ethylene glycol) triblock copolymers (Figure 2) with 3 different molecular structures, designated as PEG-PDMS-PEG[8-1-8], PEG-PDMS-PEG[8-d-8] and PEG-PDMS-PEG[1-1-1] (Rutnakornpituk, 2005; Rutnakornpituk et al.,2005; Rutnakornpituk, et al., 2006). The numbers in brackets are molecular weights (g/mol) of each block. The letter d stands for dimer of PDMS.

The suspension was prepared by mixing TiO_2 nanoparticles and dispersants in silicone oil medium using ultrasonic liquid processors, Vibra-Cell™ VC 505. All suspensions were 5 wt% solids loadings with dispersant concentration of 1% based on powder dried weight basis. The amplitude of ultrasonic was 35% and dispersion time was 4 min.

Viscosity of the suspensions prepared with PEG-PDMS-PEG[8-1-8], PEG-PDMS-PEG[8-d-8] and PEG-PDMS-PEG[1-1-1] were measured as a function of shear rates using a viscometer with small sample size adapter (Brookfield RVDV-E, E2841). Ultraviolet-visible light transmittances were measured using a UV/Vis spectrometer (Perkin Elmer Instruments, Lambda 35).

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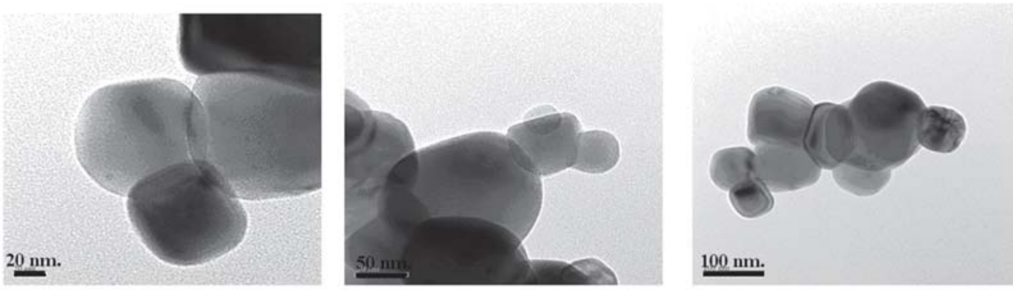

Figure 1. TEM Micrograph showing particle size and shape of as-received TiO2 powder

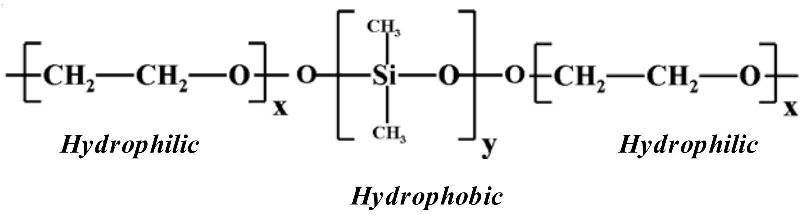

Figure 2. Molecular structure of poly(ethylene glycol-b-dimethylsiloxane-b-ethylene glycol) triblock copolymers

3. Results and discussion

3.1. Rheological behavior

As shown in Figure 3, the suspensions prepared with PEG-PDMS-PEG[1-1-1] and PEG-PDMS-PEG[8-1-8] dispersants were Newtonian. The liquid-like behavior of the suspensions indicates a high dispersion state and no flocculation. This was due to the long polydimethylsiloxane segments of PEG-PDMS-PEG[1-1-1] and PEG-PDMS-PEG[8-1-8] dispersants that extended into silicone oil medium. The long polymer chains prevented agglomeration and provided well-dispersed suspensions by increasing distance between particles.

On the other hand, The suspension prepared with PEG-PDMS-PEG[8-d-8] dispersants exhibited the decrease in viscosity with increasing shear rates. The shear thinning behavior suggested the existence of network structure or flocculation in the suspension. Since the PEG-PDMS-PEG[8-d-8] has a shorter length of polydimethylsiloxane segments comparing to PEG-PDMS-PEG[1-1-1] and PEG-PDMS-PEG[8-1-8] dispersant, particles in the suspension were at closer distance. Strong attractive particle-particle interactions caused flocculation in the system.

3.2. UV protection ability

UV protection ability of suspensions was studied by measuring degrees of transmittance at various wavelengths. As shown in Figure 4, all suspensions exhibited strong transmittance in the visible ranges and low transmittance in the UV ranges, especially in the ranges of UVB (280-320 nm). The results indicated two desired properties of the suspensions under investigation, which were transparency and UV protection ability.

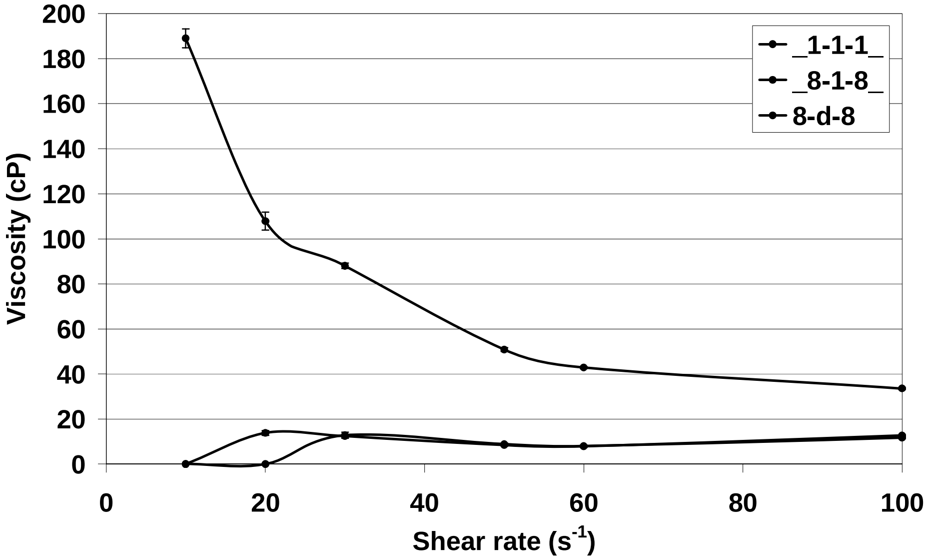

Figure 3. Shear rate dependence of viscosity for suspensions containing PEG-PDMS-PEG[8-1-8], PEG-PDMS-PEG[8-d-8] and PEG-PDMS-PEG[1-1-1] dispersants.

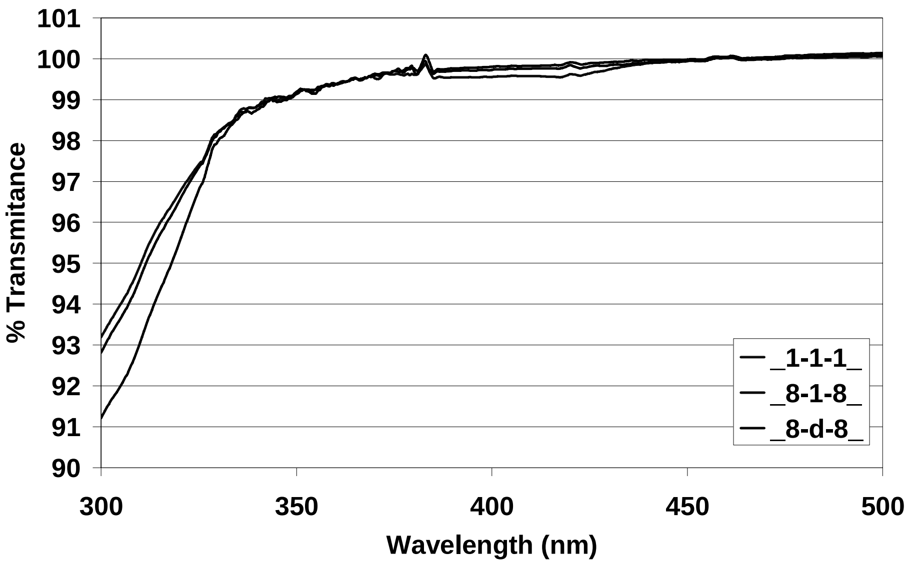

Figure 4. Wavelength dependence of transmittance for suspensions containing PEG-PDMS-PEG[8-1-8], PEG-PDMS-PEG[8-d-8] and PEG-PDMS-PEG[1-1-1] dispersants measured right after preparation.

It was known that the UV scattering power of TiO_2 increases with increasing degree of dispersion (Nasu and Otsubo, 2006). Therefore, the well-dispersed suspension prepared with PEG-PDMS-PEG[8-1-8] exhibited a strong UV protection ability while the suspension prepared with PEG-PDMS-PEG[8-d-8] dispersant showed a low UV protection ability due to flocculation.

For the suspension prepared with PEG-PDMS-PEG[1-1-1], the UV protection ability was low despite a high dispersion state suggested by the Newtonian behavior. A possible explanation was the short length of the hydrophilic polyethyleneglycol segments that caused poor attachment of the dispersant onto particle surface. Therefore, comparing to the PEG-PDMS-PEG[8-1-8] suspension, the PEG-PDMS-PEG[1-1-1] suspension might not as well-dispersed; leading to weaker UV protection ability. However, it was not sufficient so far to explain the very low UV protection ability of the PEG-PDMS-PEG[1-1-1] suspension. Further investigation in dispersion characteristics of TiO_2 particles in silicone oil medium was required for more information.

Figure 4. Wavelength dependence of transmittance for suspensions containing PEG-PDMS-PEG[8-1-8], PEG-PDMS-PEG[8-d-8] and PEG-PDMS-PEG[1-1-1] dispersants measured right after preparation.

4. Conclusions

4.1. The suspensions prepared with 1-1-1 and 8-1-8 dispersants exhibit Newtonian behavior, indicating a high dispersion state. On the other hand, the suspension prepared with 8-d-8 dispersant shows shear-thinning behavior, suggesting flocculation. The differences in rheological properties can be associated with the length of polydimethylsiloxane segments.

4.2. The well-dispersed 8-1-8 suspension provides the high UV protection ability while the flocculated 8-d-8 suspension exhibits the low UV protection.

Acknowledgement

The authors would like to thank Research unit of advanced ceramics, Department of Materials Science, Faculty of Science, Chulalongkorn University and National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials for facility and financial supports.

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