

Improvement of dispersion and stability of fine titanium dioxides in silicone fluid using poly(ethylene oxide-*b*-dimethylsiloxane-*b*-ethylene oxide) triblock copolymer: Effects of the dispersant structure and concentration

Nisanart Traiphol^{a,*}, Surachet Toommee^a, Metha Rutnakornpituk^b, Rakchart Traiphol^{b,c} and Supatra Jinawath^a

^aResearch Unit of Advanced Ceramics, Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

^bDepartment of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Naresuan University, Phitsanulok, 65000 Thailand

^cNANOTEC Center of Excellence at Mahidol University, Faculty of Science, Rama 6 Road, Ratchathewi, Bangkok 10400, Thailand

Suspensions of fine titanium dioxides were prepared in silicone fluid using newly synthesized poly(ethylene oxide-*b*-dimethylsiloxane-*b*-ethylene oxide) triblock copolymers as dispersants. The block length of the copolymers is systematically modified to allow fine tuning of the interfacial interaction between titanium dioxide particles and the silicone medium. The properties of the suspension including its rheological behavior, sedimentation rate, particle size distribution, and particle dispersion were studied. We have found that the addition of the dispersants produces suspensions with a high shear thinning behavior, leading to a high suspension stability. Improvement of the particle dispersion by the dispersants is confirmed through particle size analysis and optical microscopy. The modification of the copolymer structure also influences the particle dispersion and stability of the suspensions. The copolymer with relatively short polyethylene oxide segments produces well-dispersed and highly stable suspensions. To explain the function of the copolymers in the suspensions, particle stabilization mechanisms are suggested. This research work provides a fundamental understanding of structural-property relationships, which are important for molecular designing of polymeric dispersant for the cosmetic industry.

Key words: Suspension stability, Particle dispersion, Copolymer dispersant, Silicone fluid, Titanium dioxide

Introduction

Titanium dioxide (TiO₂) is widely used in cosmetics, skin care products, paint and coating industries. In cosmetics, TiO₂ is commonly used in sunscreens as a physical UV protecting agent due to its high refractive index, high UV protection ability, safety and stability. It has been reported to be very effective for UVB protection [1, 2]. A colloidal suspension of TiO₂ in a silicone fluid is a common form of UV protection cosmetics [1, 2]. An extensive attention moves forwards to ultrafine and nano-sized TiO₂ particles due to their physical appearance benefits of a colorless, transparent suspension when well dispersed, which reduces the residue on skin or material surfaces. However, preparation of a well-dispersed suspension of such small particles is rather difficult mainly due to the strong attractive interactions between the particles with a large surface area. To avoid particle agglomeration, effective approaches of dispersing and stabilizing are required.

Polymeric dispersants are usually added to stabilize the ultrafine particles in liquid media. To effectively

disperse and stabilize particles in a media, parts of a dispersant must adsorb on the particle surfaces while other parts extend into the media to separate particles. Therefore, the dispersant type and structure at an optimum concentration must be considered. Dispersion and stabilization of metal oxides using polymeric dispersants are extensively studied in aqueous-based systems [3-11]. However, in cosmetic applications, silicone fluids are commonly used as the media. Thus, controlling the particle dispersion and stability of silicone suspensions is a major concern. In a system of polymeric liquids such as silicone fluids, most of the studies focus on aspects of electrorheology [12-17]. There are only a few that account for particle dispersions in silicone fluids. Doi et. al. [18] studied the effects of surface treatment on rheology and flocculation of hydrophilic and hydrophobic fumed titania in silicone oils. The flocculated structures of a hydrophilic titania were found to be more compact than those of a hydrophobic one, which led to a constant viscosity at a low shear rate for the hydrophilic titania suspensions. By contrast, the interaction between isobutyl groups on the titania surfaces and the methyl groups of silicone oils caused less bulky flocculated structures in a hydrophobic titania, which led to a lower viscosity with plastic flow behavior. Bava et. al.

*Corresponding author:
Tel : +6622185541
Fax: +6622185561
E-mail: Nisanart.T@chula.ac.th

[19] reported the use of a thermoresponsive polymer to control the dispersion of hydrophilic and hydrophobic silica clusters in poly (dimethylsiloxane) (PDMS). For hydrophilic silica treated with poly(N-isopropyl acrylamide), the dispersion state was independent of temperature. However, the dispersion of polymer-treated hydrophobic silica varied with temperature.

Recently Nasu and Otsubo [20-22] investigated particle dispersions in silicone fluids using polymeric dispersants. Their studies mainly focused on the effects of the dispersant structure on the rheology and UV-protecting properties of the suspensions. Polyethylene oxide (PEO)-modified silicones of various molecular structures (i.e., comb-like, alternating block and triblock copolymers) were used as dispersants for fine titanium dioxide and zinc oxide particles in silicone oils [20, 21]. With PEO groups at the center attached to the particle surfaces and terminal groups of PDMS extended into the silicone oil medium, the PDMS/PEO/PDMS triblock copolymer was found to be an effective dispersant. Their following study investigated the influences of the PDMS/PEO/PDMS block length on the dispersant efficiency [22]. The results showed that the block length of the adsorbed segments (i.e., PEO) and the stabilizing chains (i.e., PDMS) were very important for controlling the dispersion and thus the UV-protecting ability of the suspensions. This research series mainly studied the rheology of silicone suspensions. However, further investigations regarding the stability of a suspension and the effects of dispersant concentration are necessary to completely understand the roles of polymeric dispersants on the dispersion and stabilization of particles in silicone fluids.

From the previous studies, the adsorption of PDMS/PEO/PDMS triblock copolymers on surfaces of metal oxide particles was limited when PDMS segments are too long [21, 22]. According to the authors, this problem arises from the coiling of PDMS segments around the PEO core. To reduce the effects, we introduce poly(ethylene oxide-b-dimethylsiloxane-b-ethylene oxide) triblock copolymer (PEO/PDMS/PEO) [23] as a dispersant for TiO₂ particles in silicone fluid. This class of copolymers was not investigated in the previous studies. The polar PEO segments are expected to anchor on the polar surface of TiO₂ nanoparticles while the nonpolar PDMS segments favorably interact with the silicone medium. Although less PDMS moieties compared to the previously reported PDMS/PEO/PDMS dispersant, adsorption in a train-loop-train conformation of PEO/PDMS/PEO is expected to enhance the adsorption of the polymer onto the particle surfaces. In addition, the adsorbed conformation of PEO/PDMS/PEO reduces the possibility of polymer interchain interactions, which should lead to less particle agglomeration. The PEO/PDMS/PEO copolymers with different degrees of polymerization i.e., PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 were

used to study the effects of the molecular structure on the dispersant efficiency. The difference in length of a PEO segment allows the variation of local interfacial interactions between the dispersant and particles, which affects the particle-particle interactions in the suspension. The dispersant concentrations were varied from 0-5 wt% based on solids loading. Particle dispersion and stability of the suspensions were systematically investigated through the rheological behavior, sedimentation rate, dispersion state and particle size distribution.

Material and Methods

Materials

Fine TiO₂ powder was obtained from Merck & Co., Inc., and used as received. Examination by TEM showed that the average primary particle size of the powder was about 50 nm (Fig. 1). The silicone fluid used as the medium was octamethylcyclotetrasiloxane (Sigma-Aldrich Co.) with a molecular weight of 296 g/mol and viscosity of ~20 cPs (measured at 50 rpm). Octamethylcyclotetrasiloxane was selected as a model for the silicone oil system to accelerate the sedimentation study and limit the chain entanglements caused by the medium. Therefore, the chain entanglements observed in the results were mainly caused by the dispersants. The PEO/PDMS/PEO triblock copolymers with degrees of polymerization of PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 were synthesized as described in the literature [23]. Structures of the silicone fluid medium and the copolymer dispersant are shown in Fig. 1.

Preparation and characterization of suspensions

Preparation of fine TiO₂ particles in a silicone fluid using the PEO/PDMS/PEO triblock copolymers as dispersants is schematically presented in Fig. 1. The

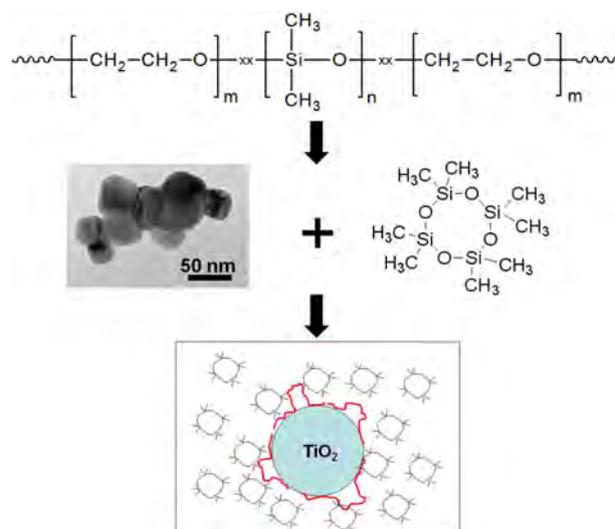


Fig. 1. Schematic for the preparation of TiO₂ nanoparticles in a silicone fluid using PEO-PDMS-PEO triblock copolymers as dispersants.

suspension was prepared by mixing fine TiO₂ particles, dispersants and silicone fluid medium using a magnetic stirrer for 5 minutes and an ultrasonic liquid processor (Sonics & Materials, Inc., Vibra-Cell™) for 7 minutes. The solids loading was 5 wt%. The dispersant concentrations were 0, 0.2, 1 and 5 wt% based on a dried powder weight basis and the copolymer dispersants were well dissolved in the silicone fluid. The rheological behavior of the suspensions was studied by measuring the viscosity as a function of shear rates using a viscometer with a small sample size adapter (Brookfield, RVDV-E). Sedimentation rates were investigated through UV transmittance measurements of the suspensions at various settling times. The particle dispersions in the suspensions was observed via optical microscopy. The suspensions were sandwiched between two glass slides. Therefore, the results reveal the actual state of the particle dispersion in the medium. Particle size distributions were analyzed by laser light scattering technique (Malvern Instruments, Ltd., Mastersizer 2000).

Results and Discussion

Effects of dispersants on the rheological behavior

The rheological behavior directly relates to the particle interaction in suspensions, which is a key to a high UV-protecting ability, high product stability and a fine appearance of UV-protecting cosmetics. The effects of the structure and concentration of the PEO/PDMS/PEO dispersant on the rheological behavior of the suspensions are illustrated in Fig. 2. While the molecular structure, i.e., the length of the PEO segment, slightly affects the rheological behavior of the suspensions, the dispersant concentration influences the degree of pseudoplastic behavior. Based on a power law model expressing the relationship between the apparent viscosity (η) and shear rate ($\dot{\gamma}$), the degree of shear thinning behavior can be determined from the

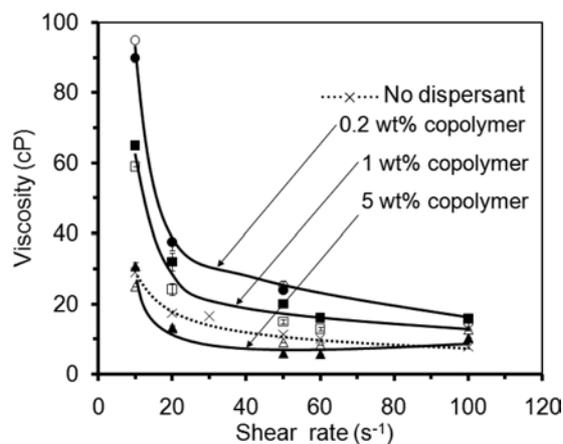


Fig. 2. Rheological behavior of TiO₂ in silicone fluid suspensions prepared with PEO-PDMS-PEO dispersants of various concentrations. Filled symbols designate suspensions using PEO23/PDMS13/PEO23 triblock copolymer and unfilled symbols designate suspensions using PEO182/PDMS13/PEO182 triblock copolymer.

flow behavior index or the shear thinning constant (n) [24]. The power law model is expressed as:

$$\eta = K(\dot{\gamma})^{n-1} \quad (1)$$

where K is the shear rate factor or consistency index. The n values for suspensions prepared with 0, 0.2, 1 and 5 wt% copolymers are 0.44, 0.23, 0.29 and 0.53, respectively. Relatively low n values of the suspensions prepared with 0.2 and 1 wt% copolymers indicate a high degree of shear thinning. The strong shear thinning behavior suggests that particles in the suspension form a 3-D network structure under a low shear condition, which prevents particles from precipitating for a period of time [25]. When the dispersant concentration is increased to 5 wt%, the suspensions exhibit relatively high n values, signifying a low degree of shear thinning similar to the suspension prepared with no dispersant. Particles tend to agglomerate and rapidly precipitate due to less gel structure to suspend them in the suspension.

Stability of suspensions

The stability of the TiO₂ in silicone fluid suspensions was studied via sedimentation experiments. Sedimentation rates of the suspensions were investigated by measuring % UV transmittance of the suspensions as a function of time. The experiments were carried out by setting a fixed position of the light beam as it passed through the suspensions. As the suspensions precipitate, there are lower numbers of particles to block the light at the point of measurement. Therefore, % UV transmittance of the suspension increases with settling times and reaches a plateau when the suspension completely precipitates. A picture describing the measurement of the sedimentation rate is shown in Fig. 3. Examples of UV transmittance spectra measured at various settling times are illustrated in Fig. 4 (a) for the suspension prepared with 0.2 wt% PEO23/PDMS13/PEO23. To investigate sedimentation rates of the suspensions, transmittance values measured at a fixed wavelength are plotted with settling times. The result is shown Fig. 4 (b) for suspensions prepared with PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 triblock copolymers at concentrations of 0, 0.2, 1 and 5 wt%. The suspension with no dispersant exhibits the highest sedimentation rate and completely precipitates within 10 minutes. The addition of 0.2 wt% dispersants significantly decreases the sedimentation rate of the suspensions. Both copolymers produce suspensions that are stable for over an hour before



Fig. 3. Demonstration of the sedimentation rate measurement.

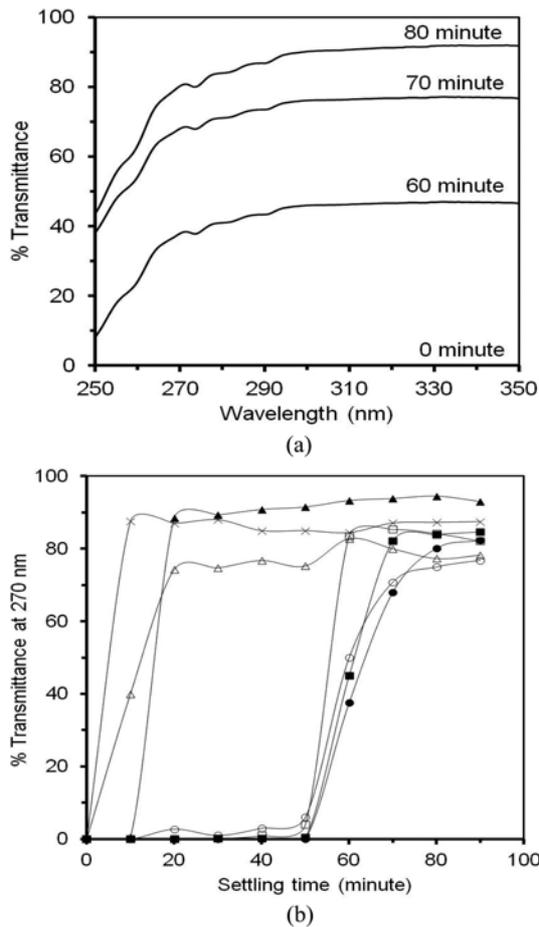


Fig. 4. (a) UV transmittance spectra of TiO_2 in a silicone fluid suspension prepared with 0.2 wt% PEO23/PDMS13/PEO23 measured at 0, 60 and 80 minutes settling times (b) Sedimentation rates of suspensions prepared with PEO23/PDMS13/PEO23 (lines with filled markers) and PEO182/PDMS13/PEO182 (lines with unfilled markers) at (x) 0 wt%, (\bullet , \circ) 0.2 wt%, (\blacksquare , \square) 1 wt% and (\blacktriangle , \triangle) 5 wt%.

completely precipitating. The suspension prepared with 1 wt% PEO23/PDMS13/PEO23 is also highly stable with a sedimentation rate similar to suspensions with 0.2 wt% dispersants. However, when PEO182/PDMS13/PEO182 is added at the same concentration, the sedimentation rate of the suspension is slightly increased. The suspension completely precipitates at 60 minutes. At a high dispersant concentration of 5 wt%, both copolymers produce suspensions with a high sedimentation rate. The unstable suspensions completely precipitate within 20 minutes. The results of the sedimentation rates are in agreement with the rheological behaviors of the suspensions. High shear thinning suspensions prepared with 0.2 and 1 wt% dispersants are highly stable while the suspensions with a low shear thinning behavior (0 and 5 wt% dispersants) rapidly precipitate.

Fig. 5 illustrates precipitation of the suspensions prepared with various concentrations of PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 triblock copolymers at settling times from 0 to 90 minutes. The

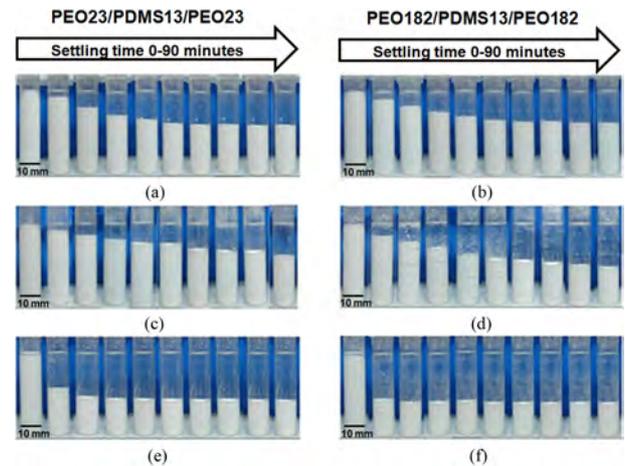


Fig. 5. Sedimentation experiment illustrates precipitation and sediment characteristics of TiO_2 in silicone fluid suspensions prepared with PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 dispersants at (a, b) 0.2 wt%, (c, d) 1 wt% and (e, f) 5 wt%.

completely precipitated periods of the suspensions are consistent with the results measured by UV spectrophotometry (Fig. 4). The sedimentation characteristics of the suspensions indicate the significance of the dispersant structure and concentration on the particle dispersion and suspension stability. At 0.2 wt% (Fig. 5 (a), (b)) and 1 wt% (Fig. 5 (c), (d)) dispersants, ratios of sediment height to initial suspension height (h/h_0) are 0.62, 0.62, 0.63 and 0.49, respectively. A high h/h_0 ratio indicates that particles are loosely packed when they precipitate and can be simply redispersed to the original dispersion states. This is caused by particle formation as loose networks under a low shear rate, which also leads to the shear thinning behavior of the suspensions. Oppositely, the suspensions prepared with 5 wt% dispersants (Fig. 5 (e), (f)) exhibit h/h_0 ratios of 0.44 and 0.42. In this case, the particles pack densely when they precipitate due to less network forming and the suspensions are extremely difficult to redisperse. The h/h_0 ratios are consistent with sedimentation rate results. Both copolymers at 0.2 wt% yield stable suspensions with similar sedimentation rates and h/h_0 ratios. At 1 wt% copolymers, the more stable suspension prepared with PEO23/PDMS13/PEO23 exhibits a higher h/h_0 ratio than the less stable suspension prepared with 1 wt% PEO182/PDMS13/PEO182. Lastly, the addition of 5 wt% copolymers results in unstable suspensions with relatively low h/h_0 ratios. Although it is difficult to directly compare our results to those reported by Nasu and Otsubo [20-22] due to the differences in the conditions of the suspension preparation, it is important to point out that, in our study, suspension stability can be significantly improved with lower dispersant concentrations.

Particle dispersion

In the previous sections, particle dispersion in the

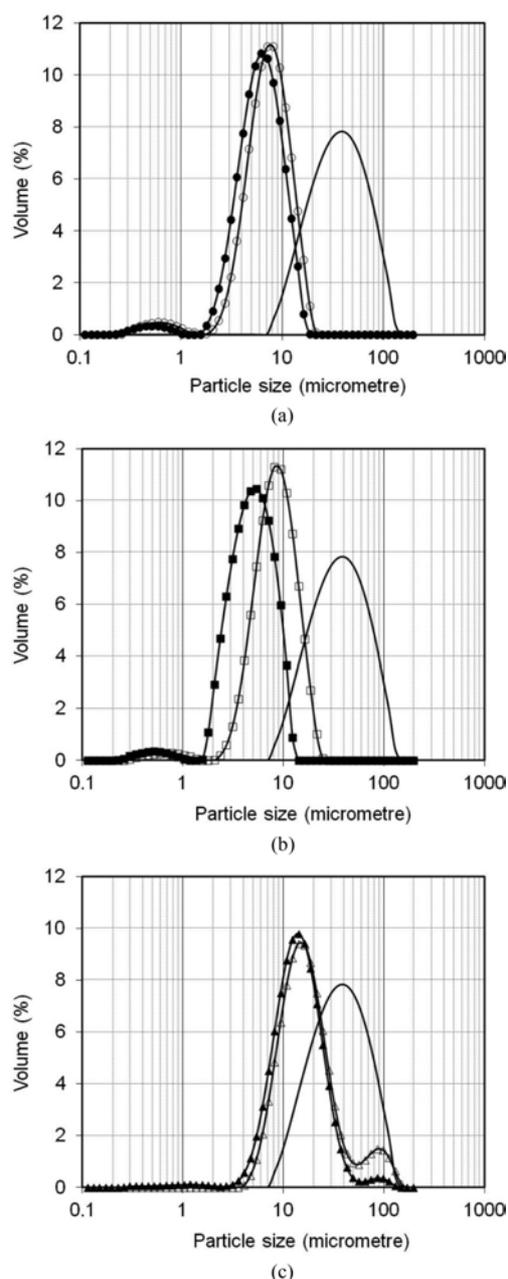


Fig. 6. Particle size distribution of TiO_2 in silicone fluid suspensions prepared without the dispersant (lines with no markers), with PEO23/PDMS13/PEO23 (lines with filled markers) and PEO182/PDMS13/PEO182 (lines with unfilled markers) at (a) 0.2 wt%, (b) 1 wt% and (c) 5 wt%.

suspensions is indicated through the rheological behavior and sedimentation results. In order to verify the state of the particle dispersion in details, direct measurement was employed. Plots of particle size distribution in Fig. 6 reveal particle dispersion state in the suspension prepared with PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 triblock copolymers at 0.2, 1 and 5 wt%. The suspension without dispersants exhibits a broad size distribution with a median diameter of $\sim 37 \mu\text{m}$, signifying a highly agglomerated state. Addition of the polymeric dispersants shifts the

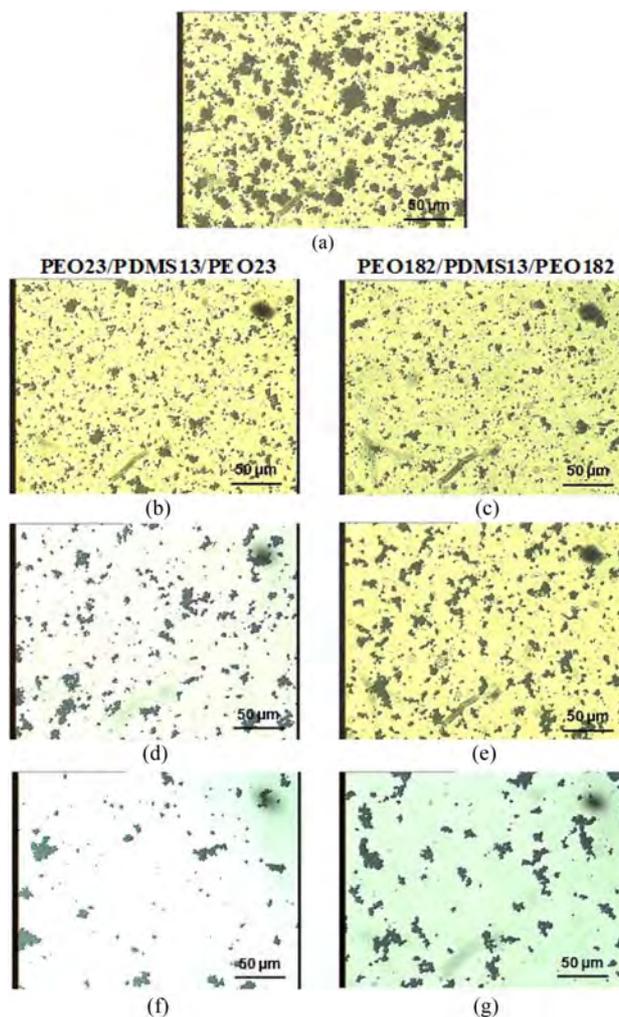


Fig. 7. Optical microscopic images showing TiO_2 particle dispersion in silicone fluid suspensions (a) No dispersant, (b) 0.2 wt% PEO23/PDMS13/PEO23, (c) 0.2 wt% PEO182/PDMS13/PEO182, (d) 1 wt% PEO23/PDMS13/PEO23, (e) 1 wt% PEO182/PDMS13/PEO182 (f) 5 wt% PEO23/PDMS13/PEO23 and (g) 5 wt% PEO182/PDMS13/PEO182.

distribution curves to a smaller size with a narrower distribution, indicating a better particle dispersion. At dispersant concentrations of 0.2 and 1 wt%, suspensions prepared with the PEO23/PDMS13/PEO23 dispersant exhibit a median particle size of $\sim 5.5 \mu\text{m}$. The median sizes of agglomerates are larger in suspensions prepared with the PEO182/PDMS13/PEO182 dispersant at the same concentrations. This further indicates that PEO23/PDMS13/PEO23 is a more effective dispersant, which is consistent with the results in the previous sections. It is important to note that small particles of less than $1 \mu\text{m}$ in size can be observed in the suspensions using a low dispersant concentration. Increasing the dispersant concentration to 5 wt%, both suspensions prepared with PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 triblock copolymers exhibit an increase in particle agglomeration. The median particle size is $\sim 17 \mu\text{m}$ and extremely large

agglomerates of greater than 50 μm can be observed, particularly in the suspension prepared with the PEO182/PDMS13/PEO182 triblock copolymer.

The corresponding optical microscopic images are illustrated in Fig. 7. Without the dispersant, agglomerates are extremely large as shown in Fig. 7 (a). Addition of the copolymer dispersants significantly decreases the agglomerate size. Using 0.2 and 1 wt% copolymers, the particle dispersion in the suspensions improves remarkably as shown in Fig. 7 (b)-(e). However, increasing the dispersant to 5 wt% (Fig. 7 (f)-(g)) results in an increase in the agglomerate size.

The dispersion state of particles clarifies the sedimentation rates of the suspensions reported in the previous section. For 0 and 5 wt% dispersants, particles are poorly dispersed. The suspensions precipitate rapidly due to the presence of large agglomerates. On the other hand, suspensions prepared with 0.2 and 1 wt% dispersants exhibit a better particle dispersion. Relatively small particles lead to highly stable suspensions.

Particle stabilization mechanism

Based on the results, adsorption of PEO/PDMS/PEO copolymers on TiO_2 surfaces and their effects on particle interactions are suggested as follows. The PEO/PDMS/PEO copolymers adsorb on the particle surface as a train-loop-train conformation. The polar PEO segments preferably anchor on the particle surfaces while the nonpolar PDMS segments extend into the silicone fluid. At concentrations of 0.2 and 1 wt% dispersants, the majority of the copolymers covers particle surfaces and provide steric stabilization for PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 dispersants, respectively. Consequently, the suspensions prepared with 0.2 and 1 wt% dispersants are well-dispersed and highly stable.

At the same dispersant concentration, the numbers of polymer chains of PEO23/PDMS13/PEO23 are 8 times greater than those of PEO182/PDMS13/PEO182. Therefore, there are more PDMS segments on the surface of particles covered with PEO23/PDMS13/PEO23. Since PDMS segments extend into the medium and provide steric stabilization, the PEO23/PDMS13/PEO23-covered particles are better dispersed as shown in Fig. 6 (a) and (b), and result in more stable suspensions as reported in Fig. 4 (b).

Increasing the concentration to 5 wt%, certain amounts of the dispersants cover the entire particle surfaces, leaving excess polymer chains in the silicone medium. The unadsorbed polymer chains are expected to be coiled at both ends (PEO segments) and stretch in the middle (PDMS segment) or formed micelles with the polar PEO in the center and PDMS stretch out in the medium. These excess polymers cause particle agglomeration by polymer bridging. The results are poor particle dispersion as shown in Fig. 6 (c), leading to unstable suspensions with a high sedimentation rate

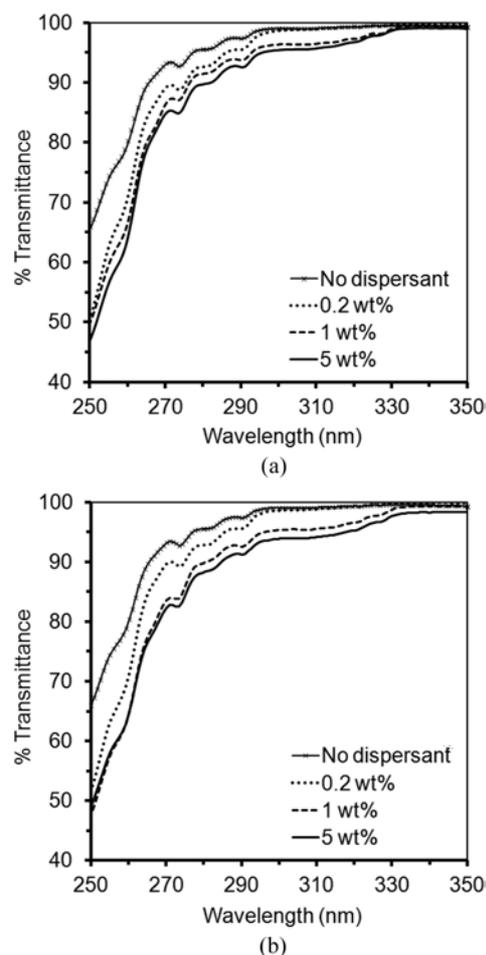


Fig. 8. UV transmittance spectra of clear supernatants obtained after centrifuged (a) solutions prepared with PEO23/PDMS13/PEO23 at various concentrations and (b) solutions prepared with PEO182/PDMS13/PEO182 at various concentrations.

as observed in Fig. 4 (b). However, the suggested particle stabilization mechanisms need further investigation.

Dispersion of TiO_2 nanoparticles

UV-protecting cosmetics desire nano-sized particles, which are able to scatter and absorb UV, and also are highly transparent in the visible range. In the previous section, the overall suspensions were investigated. However, TiO_2 nanoparticles in the suspensions cannot be examined due to obscuration from large particles. To investigate particles of nanosize, the suspensions were centrifuged at speed of 5,000 rpm for 2 minutes. Then, clear supernatants containing nanoparticles were examined by measuring the UV transmittance. Fig. 8 (a) and (b) show the UV transmittance in the range of 250-350 nm for the supernatants prepared with PEO23/PDMS13/PEO23 and PEO182/PDMS13/PEO182 dispersants, respectively. All solutions were clear with a transmittance of 100% in the visible range. The decreasing transmittance in the UV range indicates UV blocking by TiO_2 nanoparticles contained in the solutions. The solutions prepared with PEO/PDMS/

PEO dispersants exhibit a higher UV blocking ability compared to the one with no dispersant. Furthermore, increasing the dispersant concentration leads to a decrease in the UV transmittance, suggesting a greater amount of TiO₂ nanoparticles to block UV. It can be concluded from the results that PEO/PDMS/PEO dispersants promote the presence of nanoparticles in the suspensions. It is also important to note that increasing the dispersant concentration results in both the formation of large agglomerates in the suspension and an increase in nanoparticles in the supernatants.

Conclusions

PEO/PDMS/PEO triblock copolymers can be used to disperse and stabilize fine TiO₂ particles in a silicone fluid. The polar PEO segments adsorb onto particle surfaces and the nonpolar PDMS segments extend into the silicone medium. Particles are separated and stabilized in the silicone fluid via steric stabilization. At concentrations of 0.2 and 1 wt%, the dispersant produced high shear thinning, well-dispersed and highly stable suspensions. However, at 5 wt% dispersant, unadsorbed polymer chains cause particle agglomeration via polymer chain interaction, resulting in poorly dispersed and unstable suspensions. Comparing the copolymers with different structures shows that PEO23/PDMS13/PEO23 provides stronger steric stabilization than PEO182/PDMS13/PEO182. This is due to greater numbers of PDMS segments on the particle surfaces at the same dispersant concentration. In addition, the effects of the dispersants on the amount of TiO₂ nanoparticles were examined. It is found that PEO182/PDMS13/PEO182 at 5 wt% provides the highest amount of TiO₂ nanoparticles.

Acknowledgments

The authors would like to thank The Thailand Research Fund and The Office of the Higher Education Commission for research funding (Contract No. MRG5180165). The appreciation is also extended to Center of Excellence on Petrochemicals and Materials Technology and Project for Establishment of Comprehensive Center for Innovative Food, Health Products and Agriculture (PERFECTA) for their kindly supports.

References

1. A.B.G. Lansdown, A. Taylor, *Int. J. Cosmet. Sci.* 19 (1997) 167-172.
2. C. Bennat, C.C. Müller-Goymann, *Int. J. Cosmet. Sci.* 22 (2000) 271-283.
3. M. Vamvakaki, N.C. Billingham, S.P. Armes, J.F. Watts, S.J. Greaves, *J. Mater. Chem.* 11 (2001) 2437-2444.
4. K.R. Ratinac, O.C. Standard, P.J. Bryant, *J. Colloid Interface Sci.* 273 (2004) 442-454.
5. G.H. Kirby, D.J. Harris, Q. Li, J.A. Lewis, *J. Am. Ceram. Soc.* 87 (2004) 181-186.
6. J. Zhao, X. Wang, Z. Gui, L. Li, *Ceram. Int.* 30 (2004) 1985-1988.
7. N. Traiphol, *J. Ceram. Process. Res.* 8 (2007) 137-141.
8. L. Jin, X. Mao, S. Wang, M. Dong, *Ceram. Int.* 35 (2009) 925-927.
9. R. Suntako, P. Laoratanakul, N. Traiphol, *Ceram. Int.* 35 (2009) 1227-1233.
10. M. Kim, J. Jung, J. Lee, K. Na, S. Park, J. Hyun, *Colloid Surf. B-Biointerfaces* 76 (2010) 236-240.
11. N. Traiphol, R. Suntako, K. Chanthornthip, *Ceram. Int.* 36 (2010) 2011-2262.
12. Y. Komoda, T.N. Rao, A. Fujishima, *Langmuir* 13 (1997) 1371-1373.
13. X. Zhao, J. Yin, Q. Xiang, Q. Zhao, *J. Mater. Sci.* 37 (2002) 2569-2573.
14. A. Lengálová, V. Pavlínek, P. Sáha, O. Quadrat, J. Stejskal, *Colloid Surf. A-Physicochem. Eng. Asp.* 227 (2003) 1-8.
15. B. Wang, X. Zhao, *J. Mater. Chem.* 13 (2003) 2248-2253.
16. B. Wang, Y. Zhao, X. Zhao, *Colloid Surf. A-Physicochem. Eng. Asp.* 295 (2007) 27-33.
17. Y. Shang, Y. Jia, F. Liao, J. Li, M. Li, J. Wang, S. Zhang, *J. Mater. Sci.* 42 (2007) 2586-2590.
18. M. Doi, M. Kawaguchi, T. Kato, *Colloid Surf. A-Physicochem. Eng. Asp.* 211 (2002) 223-231.
19. L. Bava, D.L. Feke, I. Manas-Zloczower, S.J. Rowan, *J. Colloid Interface Sci.* 319 (2008) 160-168.
20. A. Nasu, Y. Otsubo, *J. Colloid Interface Sci.* 296 (2006) 558-564.
21. A. Nasu, Y. Otsubo, *J. Colloid Interface Sci.* 310 (2007) 617-623.
22. A. Nasu, Y. Otsubo, *Colloid Surf. A-Physicochem. Eng. Asp.* 326 (2008) 92-97.
23. M. Rutnakornpituk, P. Ngamdee, P. Phinyocheep, *Polymer* 46 (2005) 9742-9752.
24. J.S. Reed, in "Introduction to the Principles of Ceramic Processing", John Wiley & Sons (SEA) Pte. Ltd., Singapore (1989).
25. D.R. Dinger, in "Rheology for Ceramists", D.R. Dinger Publishing, Clemson, SC (2002).