

Surface Properties of Silane-Treated Titania Nanoparticles and Their Rheological Behavior in Silicone Oil

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Abstract: The surface of rutile titania nanoparticles was chemically modified by reacting with alkoxy silane. The surface and rheological properties in silicone oil having a wide range of viscosity were investigated. Total surface free energy (γ_s) of the titania particles decreased from 53.12 to 26.94 mJ/m² as the silane used for surface treatment was increased from 0 to 5.0 wt%. The surface free energy of neat silane was 25.5 mJ/m², which is quite close to that of titania particles treated with 5.0 wt% silane. Due to the hydrophobic nature of treated-titania, the contact angle was accordingly higher for polar solvent in the order of water > ethylene glycol > formamide > α -bromonaphthalene. In sum of rheological behavior, as the applied shear stress or viscosity of the silicone oil increased, the titania particles tend to form layers and agglomerated clusters, showing shear-thinning and shear-thickening behaviors, sequentially. A good dispersion of discrete titania particles obeying a Newtonian flow behavior was achieved at a surface energy or low concentration of silane-treated titania particles in hydrophobic silicone oil.

Keywords: titania, surfacemodification, surface free energy, silane, rheology.

Introduction

The behavior of concentrated particulate suspension in liquids is of importance in vast applications such as the synthesis of catalyst supports, the manufacturer of paints, and in ceramic fabrication processes. For example, in the ceramic industry, most ceramic greenware is manufactured, at least in part, using a slurry of particulate ceramic material in a solution. Since fine particles possess a large surface area, agglomeration of such particles is often encountered during processing, resulting in high viscosity and poor packing behavior at high solid content. Therefore, the formation of stable suspensions and understanding of their thermodynamic behavior are important both in industry and academia.

Titania pigments are widely used in consumer industries including paints, pigments, paper-making, and so on. Titania generally consists of an aluminium-doped rutile (Al:TiO₂) core with thin inorganic surface layers. Aluminium is impregnated into the synthetic rutile core during the production process to enhance dispersibility.¹ Dispersion of titania particles in a medium is accordingly essential for numerous applications. For concentrated particulate suspensions, rheological investigation endows a direct insight into understanding pigment dispersibility and interactions among the particles upon dispersion and processing of pigments.

Accordingly, a number of studies has been reported on the rheological behaviors of titania suspensions.²⁻⁶

A stable suspension is achieved throughout electrostatic or steric stabilization mechanism. In electrostatic stabilization, adsorbed ions build up a charged layer around the inorganic solute and aggregation is prevented by means of electrostatic repulsion.⁷ Whereas steric stabilization utilizes polymeric stabilizers, such as polyacrylic acid and polyacrylamide, for inorganic particle suspensions where aggregation is suppressed via hairy steric repulsion.⁸⁻¹² Although the latter mechanism offers low cost and high stabilizing efficiency, the incorporation of polymeric stabilizers could cause the deterioration of properties of inorganic suspensions.

To date, open literatures on the surface modification of titania and its rheological behavior have been limited. In this study, the surface of rutile titania nanoparticles were chemically modified by reacting with alkoxy silane and surface properties were studied in various polar and apolar solvents. In addition, the rheology of treated-titania nanoparticles in silicone oil mixtures having a wide range of viscosity was investigated.

Experimental

Materials. Rutile type titania particles (MT-500B, Tayca Co., Japan) having an average size of 35 nm was used as the starting material. Surface modification of titania was carried

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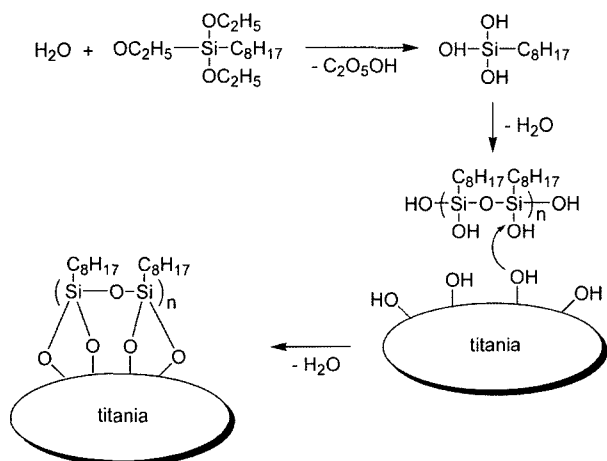
out using octyltriethoxy silane (R1-6341, Dow Corning, USA) in *n*-hexane (Daejung, Korea). Formamide (Junsei, Japan), ethylene glycol (Daejung), α -bromonaphthalene (Lancaster, England), *n*-octane (Kanto, Japan) were used as received. Two types of silicone oils, dimethicone (DC200 100CS, Dow Corning), and dimethicone (KF-96 1000CS, 10000CS, Shinetu, Japan) were used.

Sample Preparation. Procedures for the surface modification of titania particles are illustrated in Scheme I. Alkoxy silyl groups (Si-OR) in octyltriethoxy silane undergo hydrolysis with water molecules adsorbed on the titania particles to form silanols which further react with hydroxy groups existing on the surface of titania particles. On the other hand, octyl groups in octyltriethoxy silane react with silicone medium upon the preparation of suspension. Throughout these two reactions, titania, silane, and silicone oil form a chemically attached hybrid product. In the surface modification of titania, the amount of silane was varied from 0.1-5.0 wt% to obtain different degrees of hydrophobicity of titania particles. Surface modification of titania was achieved by dissolving 1.0 g octyltriethoxy silane in 20 mL *n*-hexane and stirring for 24 hrs. The resultant was filtered and washed repeatedly, then finally dried in vacuum oven at 120 °C for 12 hrs.

Suspensions of silane treated-titania particles and silicone oil having various viscosities were prepared. The amount of titania was increased up to 45 wt% with respect to a suspending medium. The suspensions were homogenized for 10 min using a homogenizer (Ultra turrax T25, Ika, Germany).

Characterizations. Contact angle between silane-treated titania particles and various liquids was measured using a capillary rise method proposed by Kilau and Pahlman^{13,14} from the following equation:

$$w^2 = c \frac{\rho^2 \gamma_L \cos \theta}{\eta} t \quad (1)$$



Scheme I. Surface modification of titania using octyltriethoxy silane.

Table I. Measurement of Geometric Factors of Titania Treated with Various Amounts of Silane

Content of Silane (wt%)	Geometric Factor, c ($\times 10^7 \text{ cm}^5$)
0	12.4
0.10	9.9
0.15	7.5
0.20	7.5
0.30	7.5
0.50	7.9
1.00	7.9
1.50	7.5
2.00	6.9
5.00	6.9

where w^2 denotes the weight gain in $[g^2]$. ρ , γ_L , and η are density, surface tension, and viscosity of a liquid, respectively. c represents a geometric factor which is related to the packing density and size of the packing material.

By rearranging the above eq. (1), one can obtain contact angle from the equation below:

$$\cos \theta = \frac{w^2 \eta}{t c \rho^2 \gamma_L} \quad (2)$$

For determining the geometric factor (Table I), octane was used as a reference liquid, and the contact angle between the solid phase and octane was assumed to be nil. Using the contact angle measured, the surface free energy was calculated from the Lewis acid/base and AB (short-range interaction) model proposed by Oss.¹⁵ In order to calculate each contribution in surface free energy such as γ_L^{LW} (Lifshitz-van der Waals interaction contribution), γ_S^+ (electron acceptor (Lewis acid) contribution), γ_S^- (electron donor (Lewis base) contribution), γ_S^{AB} (polar contribution), and γ_S (surface free energy of solid; $\gamma_S = \gamma_S^{LW} + \gamma_S^{AB}$),¹⁶⁻¹⁹ three polar solvents, formamide, ethylene glycol, and deionized water, and one apolar solvent, α -bromonaphthalene were used. The characteristics of these solvents are summarized in Table II.

Rheological properties of the titania suspensions were investigated by means of Stress Tech Rheometer (Rheologica Instrument, Sweden) using two different geometries, bob and cup, and cone and plate (plate diameter : 40 mm, cone angle: 4°). Experiments were carried out in the shear stress ranging 0.1-100 Pa at 25 °C.

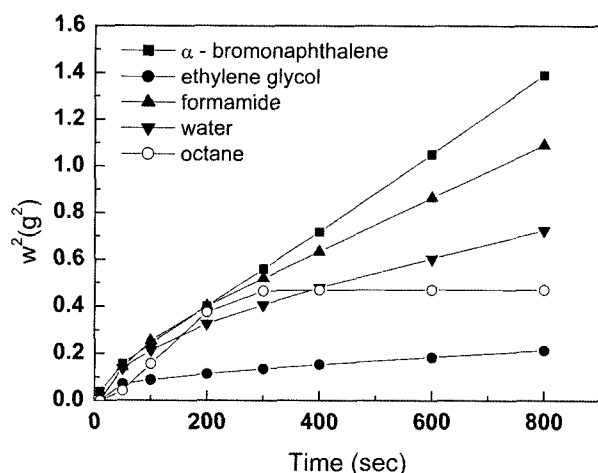
Results and Discussion

Surface Properties of Silane-Treated Titania Particles.

Figure 1 shows a representative result of weight gain of titania particles surface-modified with 0.1 wt% silane in

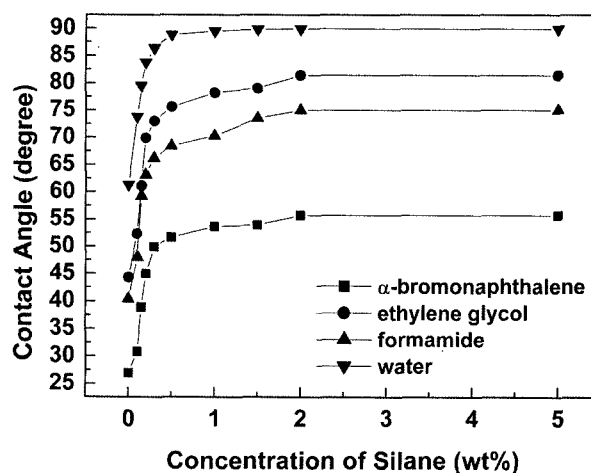
Table II. Characteristics of Solvents Used to Measure Surface Free Energy

Liquids	Parameter γ (mJ/m ²)	γ^{LW}	γ^{AB}	γ^+	γ^-	ρ (g/cm ³)	η (mPa·s)
Octane	21.8	21.8	0	0	0	0.703	0.54
α -bromonaphthalene	44.4	44.4	0	0	0	1.483	4.8
Ethylene glycol	48.3	29.3	19.0	3.0	30.1	1.113	18.3
Formamide	58.0	39.0	19.0	2.28	39.0	1.133	4.15
Water	72.8	21.8	51.0	25.5	25.5	0.998	1.002

**Figure 1.** Experimental curves of w^2 vs time for titania treated with 0.1 wt% silane.

various solvents. It is seen that the weight gain is initially rapid, and then becomes stabilized. Since the initial weight gain, i.e., greater slope in w^2 versus time, is caused by the wetting of solvents on the surface of experimental apparatus, the slope was adopted after stabilization of the weight gain. For accuracy, the experiments were conducted 8 times and average values are reported herein. The geometric factor, c , was calculated using the eq. (1). In Table II, the calculated geometric factors are listed for the titania particles treated with an increasing amount of silane in octane. The geometric factor is gradually reduced from 12.4 to 6.9 ($\times 10^7$ cm³) as the surface-modification of titania particles is achieved using an increasing concentration of silane from 0 to 5.0 wt%. It is noted that the geometric factors show the same trend in all solvents used in this study. As the surface modification of titania particles takes place, the surface free energy would decrease to result in reduced wettability, and finally to give reduced geometric factor. According to the eq. (2), the contact angle is correlated with the slope of weight gain vs time (w^2/t). Therefore, a greater contact angle is expected for the highly treated titania particles and for polar solvents.

Figure 2 represents the effect of polarity of solvents and the degree of surface modification on the contact angle. As expected, the contact angle was correspondingly higher for polar solvent in the order of water > ethylene glycol > for-

**Figure 2.** Contact angle of treated and non-treated titania with reference liquids.

mamide > α -bromonaphthalene. In a water/hydrophilic non-treated titania system, the contact angle has a high value of 61.3° since water has a high surface tension. The contact angle is abruptly increased approximately by 30° up to 0.5 wt% of silane, and leveled off for all systems. The increase in the contact angle is thought to originate from the change in the surface energy upon the surface modification of titania particles. Additionally, it is expected that a sufficient modification is achieved with 0.5 wt% of silane since the contact angle remains almost intact with a further increase in a silane concentration.

In general, hydrophobic solid materials possess a low surface free energy and vice versa. Hydrophobic solids carry hydrocarbon groups such as alkyl or phenyl, whereas hydrophilic solid surfaces have hydroxyl, carboxyl, amino, and sulfonyl groups which make them possible to easily interact with water molecules. Titania is a representative hydrophilic solid whose surface bears hydroxyl groups. Therefore, when the surface of titania particles is treated with hydrophobic silane, their surface free energies are expected to vary with the surface modification. Indeed, surface free energies are shown to closely related to the degree of silane treatment as seen in Table III. The each term in the surface energy in Table III is obtained from the Young and Dupre equations^{15,16,20,21} as follows:

$$(1 + \cos \theta) \gamma_L = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (3)$$

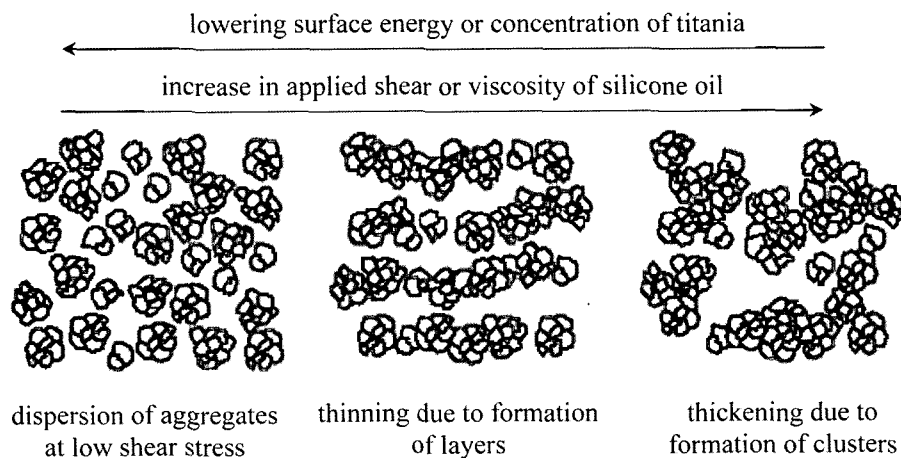
$$\gamma_S^{AB} = 2\sqrt{\gamma_S^+ \gamma_S^-} \quad (4)$$

Total surface free energy (γ_S) of titania particles accordingly decreases from 53.12 to 26.94 mJ/m² with an increase in the amount of silane used for surface treatment from 0 to 5.0 wt%. In accord with the rapid increase in the contact angle of titania particles treated with up to 0.5 wt% silane, the surface energy decreases rapidly up to 0.5 wt% silane. It is noted that the surface free energy of neat silane was measured to be 25.5 mJ/m², which is quite close to that, i.e. 26.94 mJ/m², of titania particles treated with 5.0 wt% silane. For all titania samples, the non-polar contribution of surface energy, γ_S^{LW} , is greater than the polar contribution, γ_S^{AB} by approximately 20 mJ/m². As the surface modification proceeds further, γ_S^{AB} value becomes close to zero, implying that the titania particles have hydrophobic-dominant properties instead of being hydrophilic. Furthermore, γ_S^- is much greater than γ_S^+ for titania particles, which indicates that surface modification is facilitated using a Lewis acid.

Effect of the Concentration of Treated-Titania Particles

on the Rheological Behavior. Rheological properties of a suspension are influenced by the viscosity of a medium, concentration of a solute, size and shape of solute particles, and interactions between the solute and medium (Scheme II). In current investigation, the concentration of the titania particles treated by a varying amount of silane was increased up to 45 wt%. Therefore, the concentration of titania and degree of surface modification are the variables in studying rheological behavior.

In Figure 3, the effect of surface modification of titania particles is depicted as a function of the concentration of titania particles in the suspensions. For non-treated titania in Figure 3(a), relatively low concentrations of titania particles are used since the dispersion of hydrophilic non-treated titania was difficult in a strongly hydrophobic silicone medium. In this case, non-Newtonian behavior, i.e. shear-thinning, is observed above 15 wt% of non-treated titania. Since the surface free energy of titania, 53.12 mJ/m², is much higher than that of silicone oil, 20 mJ/m², the poor dispersion of non-treated titania causes the non-Newtonian behavior arisen from shear-induced agglomeration. For 0.2 wt% silane-treated titania (γ_S of 0.2 wt% silane-treated titania: 33.80 mJ/m²) in Figure 3(b), Newtonian behavior is observed up to 30 wt%



Scheme II. Schematic diagram of the rheological behavior of titania particles in silicone oil.

Table III. Surface Free Energy Components of Treated Titania (mJ/m²)

Silane(wt%)	0	0.1	0.15	0.2	0.3	0.5	1.0	1.5	2.0	5.0
Surface E.										
γ_S^{LW}	39.90	38.50	35.20	32.41	30.14	29.32	28.31	28.15	27.21	26.77
γ_S^+	0.870	0.883	0.210	0.272	0.293	0.248	0.185	0.017	0.004	0.007
γ_S^-	15.09	6.460	6.560	4.822	4.184	3.454	3.698	4.831	5.403	5.400
γ_S^{AB} *	13.21	5.701	1.380	1.314	1.225	0.851	0.683	0.083	0.020	0.031
γ_S **	53.12	44.23	36.80	33.80	31.36	30.16	28.99	28.24	27.28	26.94

* $\gamma_S^{AB} = 2\sqrt{\gamma_S^+ \cdot \gamma_S^-}$. ** $\gamma_S = \gamma_S^{LW} + \gamma_S^{AB}$.

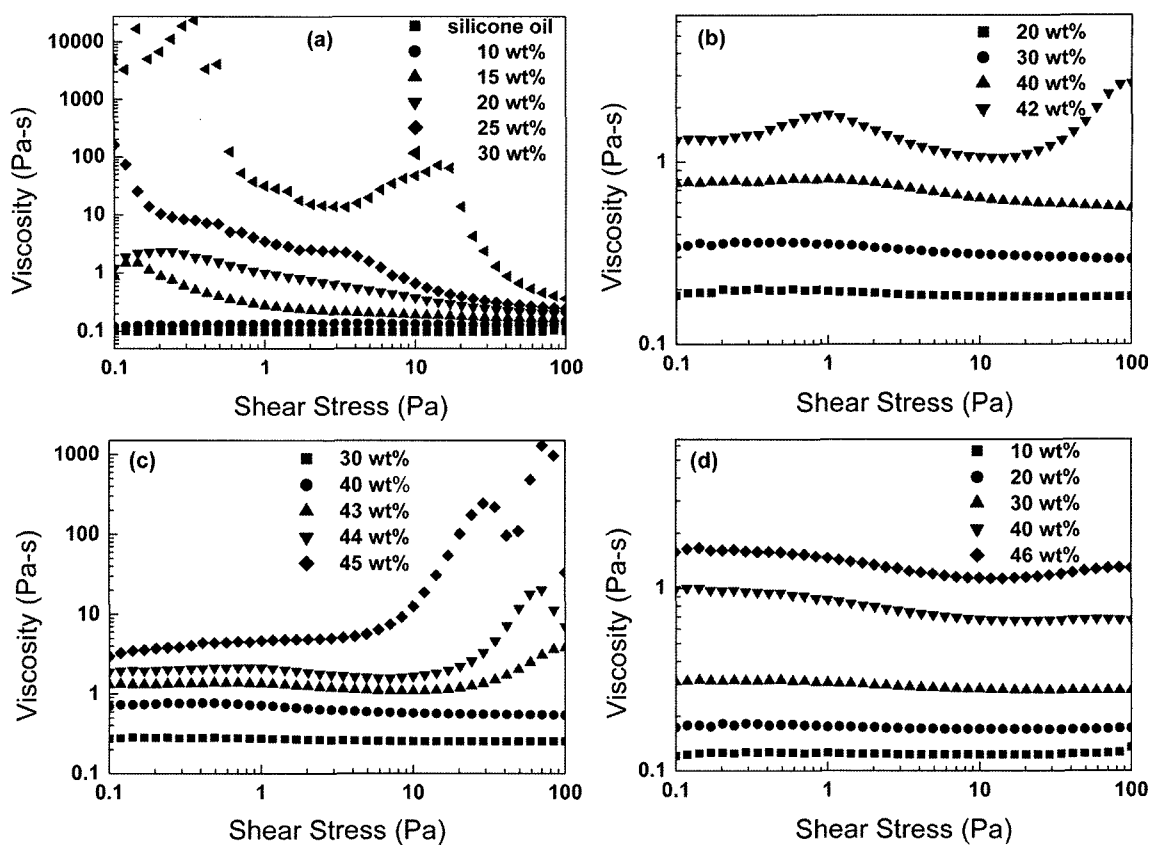


Figure 3. Viscosity vs. shear stress for (a) non-treated, (b) 0.2 wt%, (c) 1.0 wt%, and (d) 5.0 wt% silane treated titania suspensions.

of titania concentration. Above 30 wt%, instabilities due to both shear-thinning and shear-thickening are witnessed. When the titania particles are treated with 1.0 wt% silane (γ_s : 28.99 mJ/m²), Newtonian behavior is achieved up to 40 wt% of titania concentration. Above 40 wt%, the suspension shows a significant shear-thickening behavior due to the shear-induced instability. When the silane content is further increased up to 5.0 wt%, the Newtonian behavior is obtained up to a high concentration of titania particles. Even at 40 and 46 wt% suspensions, a slight shear-thinning is observed. The surface modification was sufficiently achieved with 5.0 wt% silane as seen in contact angle and surface free energy measurements. For the titania particles treated with 5.0 wt% silane, the surface energy of titania (γ_s : 26.94 mJ/m²) becomes close to that of the medium, 20 mJ/m² and the similar surface energy is believed to enhance the dispersion of solute particles in silicone oil due to the increased interactions between the discrete and continuous phases. It is worthy to mention that the slight change in the surface energy by modification of the titania surface leads to a remarkable variation in rheological properties.

In Figure 4, the concentrations of titania particles treated with increasing amounts of silane are fixed at 20, 40, and 45 wt%. In Figure 4(a), all treated-titania systems show a similar

Newtonian behavior, while a strong shear-thinning occurs for the non-treated titania. The shear-thinning behavior is caused by a substantial difference between the surface energies of non-treated titania and silicone medium. At the relatively low concentration of titania, 20 wt%, the flow characteristics seem almost identical once the titania particles are surface-modified to be hydrophobic. The result reveals that the change in the surface energy marginally affects the flow behavior once the solute particles are modified. When the concentration of titania increases to 40 wt%, overall high viscosities are obtained. More importantly, they show initial Newtonian behavior at a low shear stress region, followed by significant shear-thinning behavior for all systems. Although the surface energies of titania treated with 0.2 and 5.0 wt% silane are 33.8 and 26.94 mJ/m², respectively, the viscosities of the two sample differ only by 2 Pa·s. In Figure 4(c), the viscosities of 45 wt% titania suspension are represented. Although the surface energies of titania treated with above 2.0 wt% silane are almost similar, their flow behaviors are strikingly different, showing a sensitive shear-thickening at a high shear stress regime. These results indicate when the sufficient surface modification is achieved, it sensitively influences the flow behavior rather than surface free energy. The cause of rheological instability can be explained by

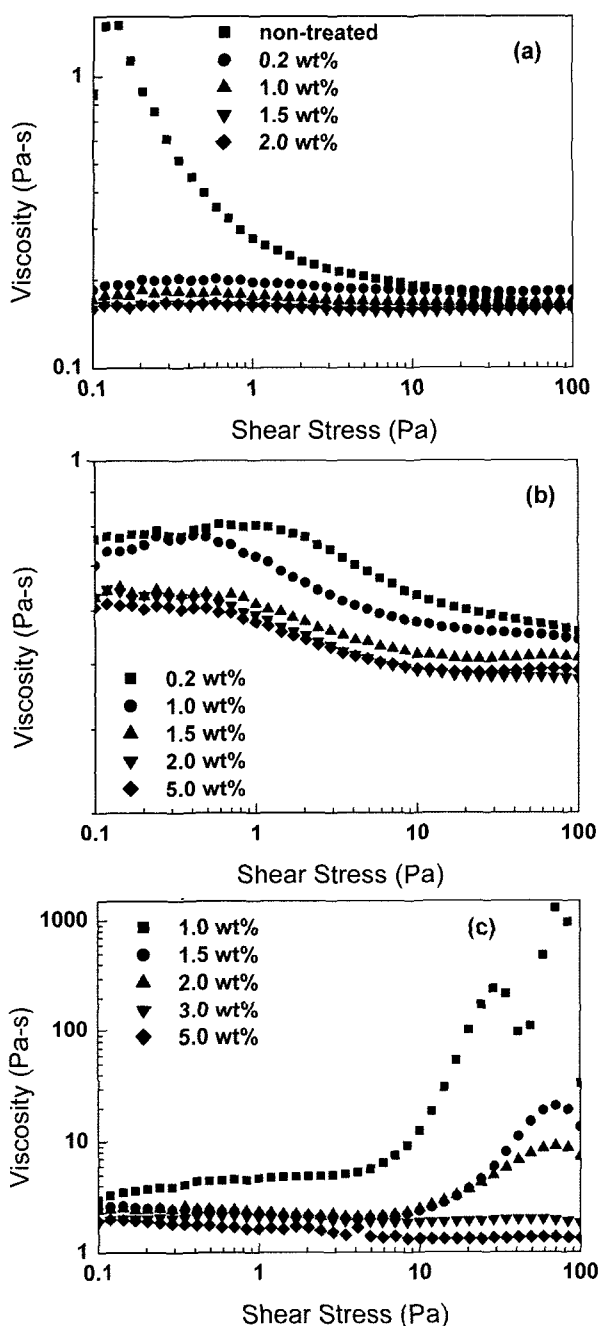


Figure 4. Viscosity vs. shear stress for suspensions including (a) 20 wt%, (b) 40 wt%, and (c) 45 wt% titania treated with a varying amount of silane.

shear-induced aggregation and agglomeration of titania particles in the medium.²²⁻²⁵

Figure 5 denotes the increase in the relative viscosity of non-treated and 5 wt% silane treated titania particles along with a Krieger-Dougherty equation²⁶:

$$\eta = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (5)$$

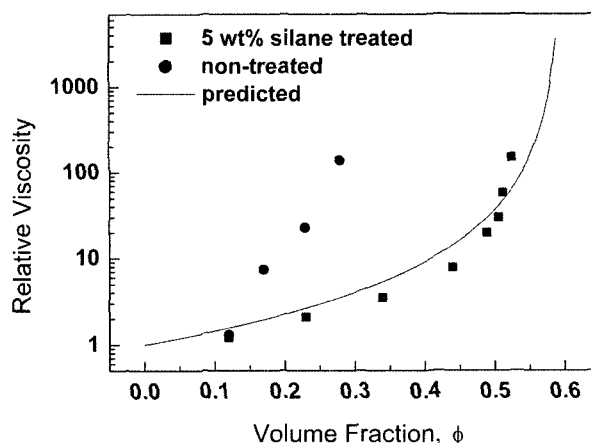


Figure 5. Relative viscosity as a function of the silane-treated or non-treated titania volume fraction. The solid line is a predicted result from Krieger-Dougherty theory.

where η is the relative viscosity (defined as the mixture viscosity divided by the viscosity of the carrier fluid, i.e., silicone oil), $[\eta]$ is the intrinsic viscosity, ϕ is the particle solids loading, and ϕ_m is the maximum solid loading. In Figure 5, the viscosity of non-treated titania suspension abruptly increases at a low volume concentration. On the other hand, the viscosity of a 5 wt% silane treated titania suspension steadily increases up to ca. $\phi = 0.5$, then rapidly overshoots. By fitting the 5 wt% silane treated titania suspension using the Krieger-Dougherty equation, $[\eta]\phi_m$ and the maximum loading (ϕ_m) are estimated to be 2.0 and 0.6, respectively. Barnes *et al.*²⁷ have reported that $[\eta]\phi_m$ of nano-sized spherical particles and relatively larger spherical particles is 1.92 and 2.0, respectively, and the corresponding maximum loading (ϕ_m) is 0.61. Our experimental results for titania particles show an excellent agreement with the reported values.

Effect of the Viscosity of Medium on the Rheological Behavior. In order to investigate the effect of viscosity of a continuous phase on the rheological behavior of titania suspensions, the medium viscosity was varied by mixing two silicone oils of 1000 CS and 10000 CS (see Table IV). Titania particles treated with 5 wt% silane were suspended in the mixture of silicone oil and the relative viscosity, defined as a ratio of the viscosity of suspension to that of the medium, is plotted in Figure 6. When the surface-modified titania particles are suspended in silicone oil at 20 wt%, Newtonian behavior is observed for all the media having different viscosities, indicating that good dispersion is achieved at this concentration. Generally, agglomeration of solute particles in a medium with a high viscosity is reduced since the mobility of the particles is limited in a high viscosity medium. On the other hand, transfer of mechanical energy during the preparation of suspension, i.e. breakup of solute clusters into discrete particles, is restricted, because there

Table IV. Viscosities of Mixture Silicone Oils

10000 CS Oil Fraction	Viscosity (Pa·s)
0	0.72
0.1	0.82
0.2	1.26
0.3	1.72
0.4	2.07
0.5	2.95
0.6	3.92
0.7	5.02
0.8	6.15
0.9	6.93
1.0	8.88

exist strong interactions between the particles, resulting in larger cluster sizes and also greater viscosity of the suspension. The latter rationale validates the high viscosity and shear-thinning behavior due to the large size of clusters for a 10000 CS suspension in Figure 2(b). When the concentration of titania was increased to 40 wt%, the preparation of suspension in a viscous silicone oil was difficult due to a poor dispersion of solute particles.

In Figure 7, flow curves of various concentrations of 5 wt% silane treated titania suspension in silicone oil having a series of viscosity are depicted. In 100 CS silicone oil in Figure 7(a), most suspensions show a Newtonian flow behavior except 46 wt% titania concentration in which slight shear-thinning and subsequent shear-thickening phenomena with increasing applied shear stress. As mentioned earlier, when the viscosity of a medium is low, breakup of solute particles is readily achieved, therefore, the increase in the concentration of titania raises the viscosity of suspension while Newtonian behavior is marginally altered. In a 2950 CS silicone oil as shown in Figure 7(c), the maximum concentration of titania is 30 wt% where the suspension follows a Newtonian law. When 10000 CS silicone oil is used, however, a significant shear-thinning is seen. These results elucidate that the highly viscous silicone oil is unfavorable for the preparation of titania suspension due to the agglomeration of solute particles, finally resulting in a non-Newtonian flow behavior. In sum of rheological behavior, as the applied shear stress or viscosity of silicone oil increases, the titania particles tend to form layers and agglomerated clusters, showing shear-thinning and shear-thickening behaviors, sequentially. A good dispersion of discrete titania particles obeying a Newtonian flow behavior is achieved at the surface energy or low concentration of silane-treated titania particles in hydrophobic silicone oil.

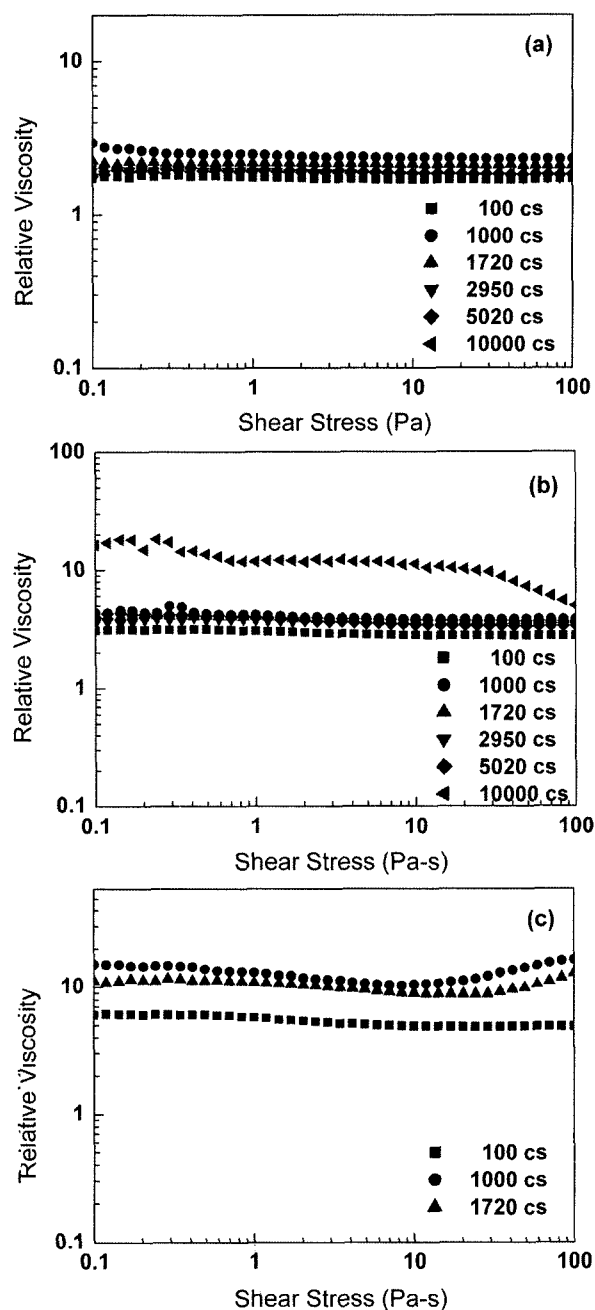


Figure 6. Relative viscosities of (a) 20 wt%, (b) 30 wt%, and (c) 40 wt% titania suspensions in various mixtures of silicone oil.

Conclusions

In this study, the surface of rutile titania nanoparticles were chemically modified by reacting with octyltriethoxy silane and surface properties were investigated. And the rheology of treated-titania nanoparticles in silicone oil mixtures having a wide range of viscosity was examined. Silane content was increased to 5 wt% relative to titania particles.

Total surface free energy (γ_s) of titania particles decreases

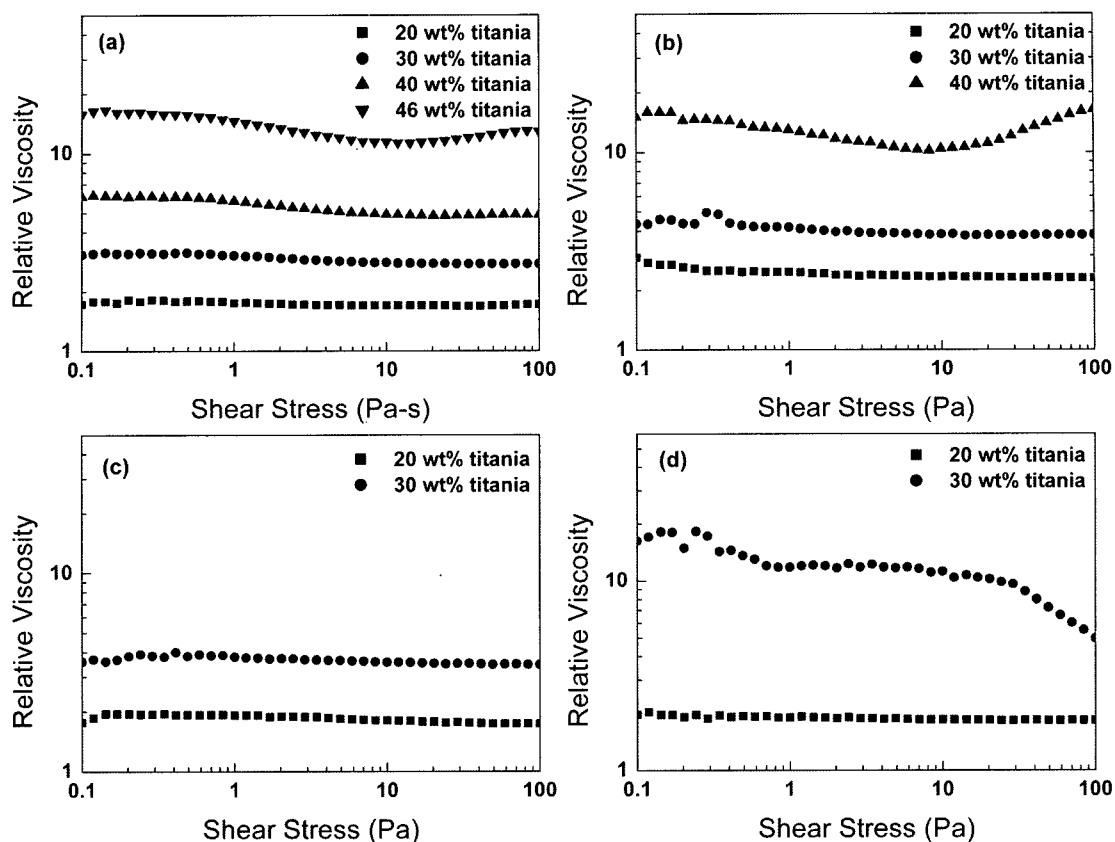


Figure 7. Relative viscosities of 5 wt% silane treated titania suspensions in silicone oils having various viscosities. (a) 100 CS, (b) 1000 CS, (c) 2950 CS, and (d) 10000 CS.

from 53.12 to 26.94 mJ/m² with an increase in the amount of silane used for surface treatment from 0 to 5.0 wt%. The surface free energy of neat silane was measured to be 25.5 mJ/m², which is quite close to that, i.e. 26.94 mJ/m², of titania particles treated with 5.0 wt% silane. For all titania samples, the non-polar contribution of surface energy, γ_s^{LW} , is greater than the polar contribution, γ_s^{AB} by approximately 20 mJ/m². As the surface modification proceeds further, γ_s^{AB} value becomes close to zero, implying that the titania particles have hydrophobic-dominant properties. As expected, the contact angle was accordingly higher for polar solvent in the order of water > ethylene glycol > formamide > α -bromonaphthalene. The contact angle was abruptly increased approximately by 30° up to 0.5 wt% of silane, and leveled off for all systems. Based on the contact angle and surface free energy measurements, it is thought that a sufficient modification is achieved with 0.5 wt% of silane since the contact angle remains almost intact with a further increase in silane concentration.

For non-treated titania, a non-Newtonian behavior is observed even at a low concentrations of titania. These non-Newtonian behaviors of shear-thinning and shear-thickening, were suppressed with an increase in the degree of surface modification. At a relatively low concentration of titania, the

flow characteristics seem almost identical once the titania particles are surface-modified to be hydrophobic. The result reveals that the change in the surface energy marginally affects the flow behavior at a low concentration once the solute particles are modified. However, the slight change in the surface energy sensitively influences the flow behavior at a high concentration of titania. When the viscosity of a suspending medium is high, a significant shear-thinning is seen even at a moderate concentration of titania since the breakup of solute particles is difficult. In sum of rheological behavior, as the applied shear stress or viscosity of silicone oil increases, the titania particles tend to form layers and agglomerated clusters, exhibiting shear-thinning and shear-thickening behaviors, sequentially. A good dispersion of discrete titania particles obeying a Newtonian flow behavior is achieved at the low concentration or surface energy of silane-treated titania particles in hydrophobic silicone oil.

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