

Detrimental Thixotropic Thinning of Filter Cake of $\text{SiO}_2\text{--Al}_2\text{O}_3$ Composite Coated TiO_2 Particles and Its Control

Bing-Xin Wei, Lin Zhao, Ting-Jie Wang,* and Yong Jin

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

ABSTRACT: A $\text{SiO}_2\text{--Al}_2\text{O}_3$ double layer coating process is widely used for TiO_2 particle to reduce its photocatalytic activity. The conventional coating process needs a long time and uses large amounts of acid and alkali solutions. We recently developed a new $\text{SiO}_2\text{--Al}_2\text{O}_3$ composite coating process that needs less time and does not use acid and alkali solutions. This process produced coated TiO_2 particles with excellent weather durability, but it had the problem that the filter cakes composed of these particles were thixotropically thin and were easily broken up by shear or disturbance on a conveyor belt; that is, the cakes thinned into slurries very quickly. A slurry is not a suitable physical form for the subsequent drying process in industrial production. To understand this problem better, the rheology of the filter cakes was measured. Experiments to investigate the mechanism of the thixotropic thinning behavior indicated that the Si–O–H groups on the surface of the coated particles formed, by hydrogen bonding, a network structure of the particles that entrapped water within the structure. This structure was easily destroyed by an applied shear or disturbance, leading to the release of the occluded water, and the presence of water caused the cake to become a slurry and its viscosity to decrease sharply. This thixotropic thinning behavior of the filter cake was eliminated by coating the particle surface with a thin film of aluminum oxide.

1. INTRODUCTION

Titanium dioxide particle is the best white pigment available. It is widely used in the paint, plastic, and paper industries because of its excellent optical properties, nontoxicity, and chemical inertness. However, titanium dioxide particle must be properly coated to increase its weather durability.^{1,2} Many metal oxides such as SiO_2 , Al_2O_3 , ZrO_2 , Fe_2O_3 , and ZnO have been used as coating materials. In industrial production, a $\text{SiO}_2\text{--Al}_2\text{O}_3$ double layer coating process is widely used.^{3–5}

However, the conventional $\text{SiO}_2\text{--Al}_2\text{O}_3$ double layer coating process needs a long time and uses massive amounts of acid and alkali solutions. To improve on this conventional coating process, we have developed a new $\text{SiO}_2\text{--Al}_2\text{O}_3$ composite coating process in which a 2 h neutralization reaction of the coating agents, Na_2SiO_3 and $\text{Al}_2(\text{SO}_4)_3$, was used instead of the 6 h needed for the old process (2 h reaction of Na_2SiO_3 and H_2SO_4 plus 2 h reaction of $\text{Al}_2(\text{SO}_4)_3$ and NaOH plus 2 h aging process between these two reactions). This new process needs only half of the time and eliminates the consumption of acid and alkali solutions. Also, it is easier to operate because the pH does not have to be controlled. The composite coated TiO_2 particles produced in the new process also have excellent weather durability. However, the filter cake composed of these particles thins (“thin” is used in this work with the meaning of becoming less viscous) on the conveyor belt, and it would collapse into a slurry very quickly. Once the filter cake becomes a slurry, the subsequent drying step cannot be performed because the flash dryer is designed to use filter cakes.

The problem is, why was the filter cake thixotropic; that is, why did it exhibit a rapid thinning behavior when subjected to a small shear or disturbance? It has been reported in the literature that the composition, particle size, and solution pH are some of the important factors that lead to the particles having different slurry

viscosities and that these factors act through the forming of a network structure of the particles.⁶ The surface of the particles also affects the slurry viscosity of the particles.⁷ Liddell et al.⁸ reported that TiO_2 particle slurries have different viscosities in different filtration devices under different compression forces. Many studies^{7–9} have reported that the ζ potential is an important factor in the rheology of shear thinning. When the slurry pH is near the isoelectric point of the particles, the surface charge density on the particles is close to zero and the electrostatic repulsive force due to particles with the same charge is very small or absent. In this case, attractive van der Waals forces dominate, which leads to interparticle attraction and aggregation. It has also been reported that the water contained within flocculated particles is easily drained by a shear or disturbance, whereupon the flocculated structure is destroyed.^{7–9}

This work is a study of the rheological behavior of slurries of titanium dioxide particles that have been coated with different layers. The mechanism of the shear-induced thinning process and a suggestion for the control of the thixotropic thinning behavior are given.

2. EXPERIMENTAL SECTION

2.1. Reagents. Commercial TiO_2 particles from the sulfate process, in which TiO_2 particles were produced by the hydrolysis of TiOSO_4 and a subsequent calcination, were used in the experiments. The TiO_2 particles had the rutile structure and a

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Table 1. Coating Procedures of Different Samples

samples		coating procedures		
(1) SiO ₂ –Al ₂ O ₃ double layer coating	3% SiO ₂	aging	2% Al ₂ O ₃	aging
(2) SiO ₂ –Al ₂ O ₃ composite coating	3% SiO ₂ + 2% Al ₂ O ₃	aging		
(3) Al ₂ O ₃ modified composite coating	3% SiO ₂ + 2% Al ₂ O ₃	aging	0.5% Al ₂ O ₃	aging
(4) SiO ₂ modified composite coating	3% SiO ₂ + 2% Al ₂ O ₃	aging	0.5% SiO ₂	aging
(5) Al ₂ O ₃ single layer coating	2% Al ₂ O ₃	aging		
(6) SiO ₂ single layer coating	3% SiO ₂	aging		

mean diameter of 300 nm. All chemicals used were analytical reagent (AR) grade.

2.2. Coating. Coating experiments were conducted in a flask with the temperature and pH measured online with a thermometer and pH meter. TiO₂ particles at a concentration of 500 g/L (250 g of TiO₂ particles + 500 g of water) were dispersed in deionized water by a continuous ultrasonic treatment for 30 min.

(1) For the SiO₂–Al₂O₃ double layer coating, 1.29 mol/L Na₂SiO₃ solution and 10% H₂SO₄ solution were simultaneously titrated into the TiO₂ suspension. The TiO₂ suspension was stirred vigorously and it was controlled at pH 9 by peristaltic pumps by the adjusting of the titration rate of the H₂SO₄ solution while keeping the titration rate of the Na₂SiO₃ solution constant. The temperature was controlled by a constant-temperature water bath at 60 °C. This process was performed for 2 h for the coating amount of 3 wt % (SiO₂:TiO₂). After titration, the suspension was aged for 2 h under stirring. Then, 0.50 mol/L Al₂(SO₄)₃ solution and 4.5 mol/L NaOH solution were simultaneously titrated into the TiO₂ suspension at a constant of pH 5, at a temperature of 60 °C, and with 2 wt % (Al₂O₃:TiO₂) coating amount by adjusting the titration rate of the NaOH solution with a constant titration rate of the Al₂(SO₄)₃ solution. The suspension was then aged for another 2 h under stirring.

(2) For the SiO₂–Al₂O₃ composite coating, 1.29 mol/L Na₂SiO₃ solution with a set amount of NaOH and 0.50 mol/L Al₂(SO₄)₃ solution were both simultaneously titrated into the TiO₂ suspension at constant rates at 60 °C. The coating amounts of SiO₂ and Al₂O₃ were controlled to be 3 wt % (SiO₂:TiO₂) and 2 wt % (Al₂O₃:TiO₂), respectively. The slurry pH was not controlled, and it decreased from about pH 10 to pH 5. After the titration, the suspension was aged for 2 h under stirring.

(3) For the Al₂O₃ modified composite coating, the SiO₂–Al₂O₃ composite coating process was the same as item 2. After the 2 h aging process, 0.5 wt % Al₂O₃ was coated at pH 5 and a temperature of 60 °C by the method in item 1. Then the suspension was aged for 0.5 h under stirring.

(4) For the SiO₂ modified composite coating, the SiO₂–Al₂O₃ composite coating process was the same as item 2. After the 2 h aging process, 0.5 wt % SiO₂ was coated at pH 9 and a temperature of 60 °C by the method in item 1. Then the suspension was aged for 0.5 h under stirring.

(5) For the Al₂O₃ single layer coating, 2 wt % Al₂O₃ was coated at pH 5 and a temperature of 60 °C by the method in item 1. Then the suspension was aged for 2 h under stirring.

(6) For the SiO₂ single layer coating, 2 wt % SiO₂ was coated at pH 9 and a temperature of 60 °C by the method in item 1. Then the suspension was aged for 2 h under stirring.

For a quick reference, the above coating procedures are summarized in Table 1.

The coated TiO₂ particles were filtered and washed repeatedly using a vacuum pump (this is similar to the process with a plate

and frame filter press in industrial production). Then, the filter cakes were dried at 105 °C for 24 h.

2.3. Characterization. A high-resolution transmission electron microscope (HRTEM, JEM-2011, JEOL, Tokyo, Japan) was used to examine the surface morphology of the particles. The physical adsorption of N₂ (Autosorb-1-C, Quantachrome, Boynton Beach, FL, USA) was used to determine the particle surface area and pore size distribution. An infrared spectrometer (FTIR Nicolet 5700, Thermo Nicolet, Madison, WI, USA) was used to characterize the chemical bonds. The solid volume fraction of coated TiO₂ particles in the sample was calculated by the particle mass, concentration, and average density. The rheological behavior was measured by a rotary rheometer (Physica MCR 301, Anton Paar, Österreich, Austria) using samples of filter cakes and slurries with different solid volume fractions. ζ potentials of particles with different values from pH 2 to pH 11 were measured with a ζ potential analyzer (ZetaPALS, Brookhaven, Holtsville, NY, USA).

3. RESULTS AND DISCUSSION

3.1. Surface Structure. Figure 1 shows the surface morphology of the coated TiO₂ particles. Continuous and dense films of about 5 nm thickness on the surface of the ~300 nm particles were obtained in both the double layer coating process and composite coating process. No difference between the two coating layers was seen even at the nanometer scale. The specific surface areas of the double layer coated and composite coated particles were 8.35 and 12.92 m²/g, respectively, while that of uncoated TiO₂ particles was 6.81 m²/g. The pore size distributions of the particles from the two coating processes are shown in Figure 2. The pore sizes of the particles from both coating processes were nearly the same, with a dominant peak at 0.5 nm. The coating can be considered a pore-free film.

Infrared spectra for the particles from the two coating processes are shown in Figure 3. For comparison, samples of single layer coatings of Al₂O₃ and SiO₂ are also shown in Figure 3. For the uncoated TiO₂ particles, the peaks at 3400 and 650 cm⁻¹ were assigned to the O–H and Ti–O vibrations. For the single layer Al₂O₃ coated particles, a peak at 1100 cm⁻¹ from the Al–O vibration appeared, and for the single layer SiO₂ coated particles, the peaks at 1050 and 1200 cm⁻¹ were assigned to Si–O vibrations. For the double layer coated particles, the peaks at 1050 and 1200 cm⁻¹ were analyzed to be a superposition of the Al–O and Si–O vibrations, indicating that the structure of the coat formed was that of a layer of SiO₂ and then a layer of Al₂O₃. However, for the composite coated particles, there were new peaks at 1100 and 950 cm⁻¹, which showed that Al–O–Si and Si–O–Si bonds were formed.¹⁰ This meant that the composite coating process formed a coated surface of aluminosilicate.

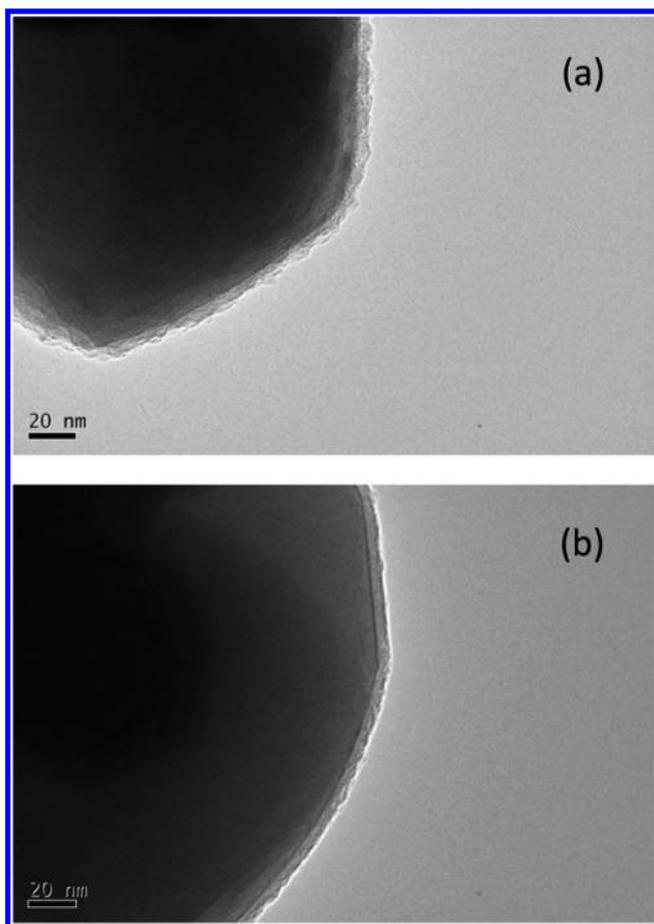


Figure 1. HRTEM images of the surface morphology of TiO_2 particles that were (a) double layer coated and (b) composite coated.

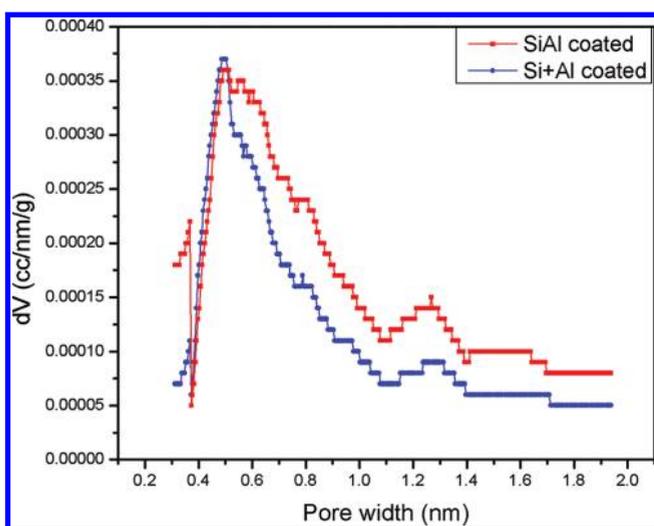


Figure 2. Pore size distribution of the double layer coated (Si+Al) and composite coated TiO_2 particles (SiAl).

The aluminosilicate is a three-dimensional structure formed by corner-sharing tetrahedrons of SiO_4^{-4} and AlO_4^{-5} .^{11–13}

3.2. Thixotropic Thinning Behavior. As distinct from the filtration performed in industry, the filtrating in the experiments

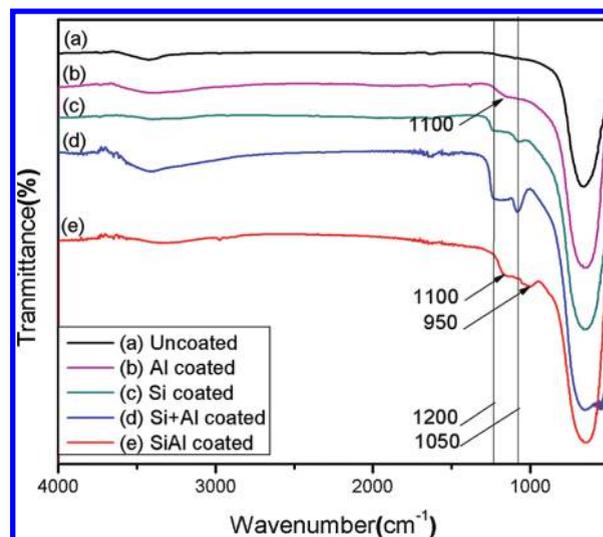


Figure 3. Infrared spectra of uncoated TiO_2 particles and particles coated with Al_2O_3 (Al), SiO_2 (Si), double layer film, and composite film.

was performed by vacuum filtration. After vacuum filtration, both of the filter cakes of the double layer coated and composite coated particles appeared very dry, but the latter cake rapidly disintegrated when it was touched and it changed from a solid-like to a slurry-like texture, while the filter cake of the former was little changed by touch. The filter cake of the latter particles could be characterized as thixotropic; that is, it was solid-like at rest but would flow under stress.¹⁴ The experiments to examine the slurry-like cake comprising the composite coated particles showed that it turned back to be solid-like again after about 2 h. There is a need to understand what happened during the change from being solid-like to slurry-like because this affects the drying process in the production process.

The viscosities of the two filter cakes comprising the double layer coated and composite coated particles were measured with a rotating rheometer. The thixotropic thinning behavior, that is, the change from being solid-like to slurry-like, of the cake made up of the composite coated particles was a rapid process that occurred very quickly once a shear or disturbance had acted on the cake, so this phenomenon was difficult to characterize. Figure 4 shows the different rheological behavior of the two filter cakes. The cake composed of the double layer coated particles showed a typical shear thinning behavior. The viscosity changed gradually as the shear rate increased. However, the cake made of the composite coated particles had already completed its rapid change of texture at the beginning of the measurement, and its viscosity rapidly decreased to be only about 1% of that of the other cake. The data in Figure 4 were obtained with the solid volume fractions of double layer coated particle cake at 25.5% and that of the composite coated particle cake at 20.9%. It had been reported that the solid volume fraction affects the slurry viscosity.¹⁵ However, Figure 4 indicated that it was not only the viscosities of the filter cakes that were different but also their rheological behavior, i.e., their shear thinning and thixotropic thinning.

For further study of the influence of the solid volume fraction, the solid volume fractions of the two cakes were changed by adding 10, 30, and 50 wt % water. The corresponding solid volume fractions of the double layer coated particle samples were 21.2, 15.8, and 12.7%. The solid volume fractions of the

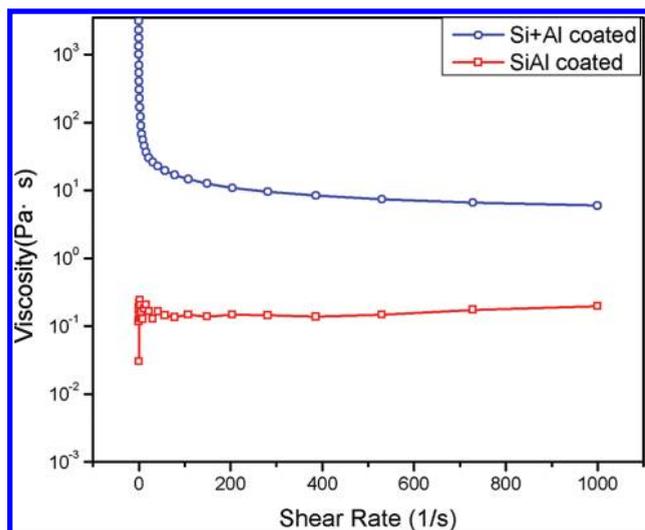


Figure 4. Rheology of filter cakes of double layer coated TiO_2 particles and composite coated TiO_2 particles.

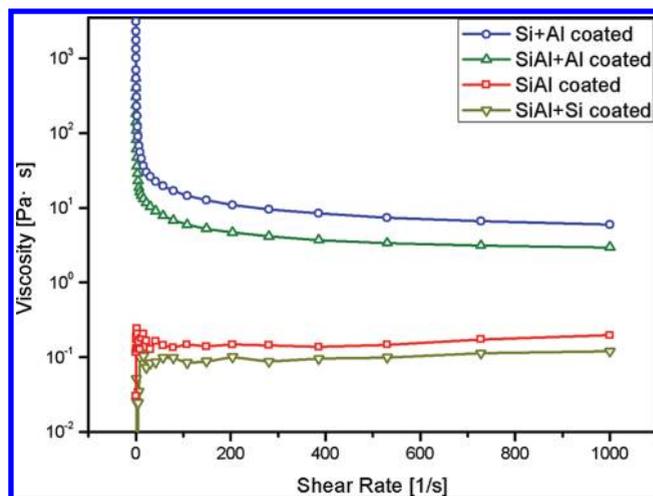


Figure 6. Rheology of filter cakes of coated TiO_2 with different surface coats.

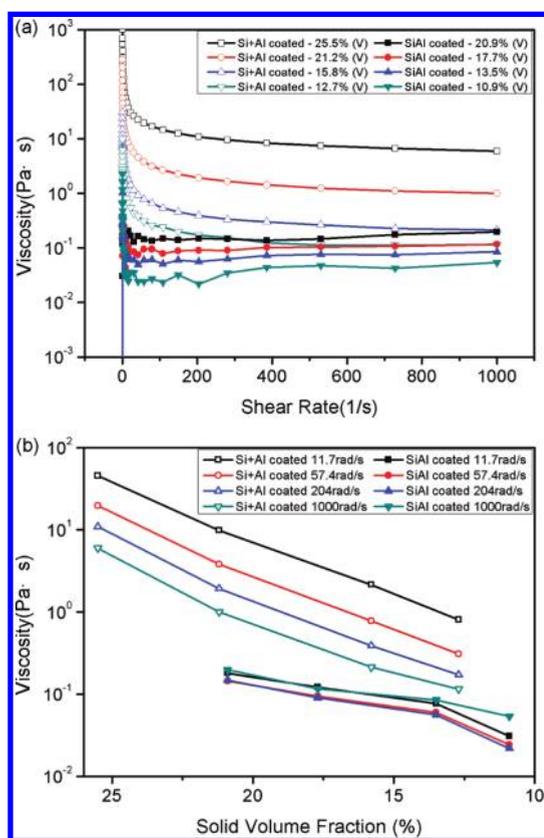


Figure 5. Viscosity of slurries of double layer coated and composite coated TiO_2 particles as a function of (a) different shear rate and (b) different solid volume fractions.

composite coated particle samples were 17.7, 13.5, and 10.9%. The rheologies of these slurries were measured, and these are shown in Figure 5a. The slurries of the double layer coated particles at different solid volume fractions showed a similar rheology of shear thinning, with the viscosity decreasing as the shear rate increased. The slurries of the composite coated particles at different solid volume fractions also showed a similar

rheology of thixotropic thinning, which was a rapid and large viscosity decrease, and then the resulting much smaller viscosity changed little with shear rate increase.

To show these features more clearly, the slurry viscosity change versus solid volume fraction at the selected shear rates of 11.7, 57.4, 204, and 1000 rad/s are shown in Figure 5b. The slurry viscosities of both the double layer coated and composite coated particles decreased as the solid volume fraction decreased. However, the slurry viscosity of the double layer coated particles was much higher than that of composite coated particles at the same solid volume fraction. The difference in viscosity was smaller as the solid volume fraction became less. The slurry viscosities of the double layer coated and composite coated particles became close at a low solid volume fraction. To further confirm that the thixotropic thinning behavior of the filter cake of the composite coated particles was not due to an influence of the solid volume fraction, slurries at different solid volume fractions of 10.7, 16.7, 25.0, and 37.5% were prepared from the dried powders of the above two cakes. These slurry rheologies were also measured, and they showed the same trends as the slurries made by adding water to the filter cakes.

Therefore, it can be concluded that the solid volume fraction was not the key factor causing the difference in the rheology of the slurries. It is probable that a difference on the surfaces of the coated TiO_2 particles was the main factor causing the difference in the rheology of the filter cake.

3.3. Control of the Thixotropic Thinning Behavior. The above analysis indicated that it was most probably the surface of the particles that determined the filter cake rheology. Experiments were designed that made use of a coating of 0.5 wt % Al_2O_3 on the particles with the composite coating to make the particle surface the same as that of the double layer coated particles. The cake rheologies of the double layer coated and composite coated particles, as well as those of the 0.5 wt % Al_2O_3 modified composite coated particles, are shown in Figure 6. The changing of the surface of the composite coated particles where it was coated with a thin layer of Al_2O_3 changed the cake rheology, which became similar to that of the double layer coated particle cake. After this surface change, the thixotropic thinning phenomenon of the filter cake did not occur. The slurry viscosities of

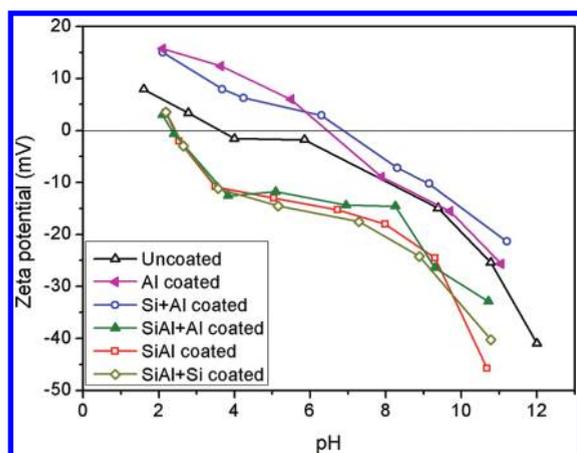


Figure 7. ζ potential of coated TiO_2 particles with different surface coats.

the composite coated particles modified to have an Al_2O_3 coat at different solid volume fractions were also measured. They showed the same shear thinning behavior as those of the double layer coated particles. This showed that the filter cake rheology can be significantly changed by changing the particle surface. It should be mentioned that the Al_2O_3 modified composite layer coating process still has the advantages of high efficiency, low consumption, and easy operation.

For comparison, the composite coated particles were also modified by coating with 0.5 wt % SiO_2 . The cake rheology of these particles is also shown in Figure 6. The cake made up of these modified particles also showed the same thixotropic thinning behavior of the composite coated particle cake.

3.4. Analysis of the Thixotropic Thinning Behavior. The ζ potentials of the different samples were measured to study their effects on the rheology. The measurement errors of ζ potential were about $\pm 10\%$. Figure 7 shows the ζ potential change for values from pH 2 to pH 11 for uncoated TiO_2 particles, double layer coated particles, composite coated particles, Al_2O_3 coat modified composite coated particles, and single layer Al_2O_3 coated particles. The isoelectric point for the uncoated TiO_2 particles was 4.2, which was consistent with two values reported in the literature^{3,16} and slightly less than the value of 4.9 reported by Morris et al.¹⁷ The difference may be due to sample difference and measurement uncertainties. The isoelectric point of the double layer coated particles was about 7, which was also in good agreement with values reported in the literature.¹⁷ This was nearly the same as that of the single layer Al_2O_3 coated particles. When 0.5 wt % Al_2O_3 was coated on the composite coated particles, its isoelectric point was 2.7, which was nearly the same as that of the original composite coated particles. Our previous work¹⁸ had shown that the ζ potential does not change much when the coating amount is less than 0.5 wt % Al_2O_3 . Since the thixotropic thinning behavior of the filter cake was prevented with the Al_2O_3 coating of the composite coated particles, and the 0.5 wt % Al_2O_3 coating layer did not change the ζ potential significantly, it was inferred that the ζ potential was not the main cause of the rapid thinning behavior.

Figure 6 shows that the filter cake rheology with a SiO_2 surface was quite different from that with an Al_2O_3 surface, while its isoelectric point was also measured to be 2.7 (see Figure 7), which is the same as that of the composite coated particles with a 0.5 wt % Al_2O_3 coat. To further confirm that it was the SiO_2

surface that mainly caused the thixotropic thinning behavior in the cake rheology, particles with a single layer of 2 wt % SiO_2 coat were prepared and shown to have the same rheology; that is, its filter cake had the thixotropic thinning behavior as the cake of the composite coated particles. These results confirmed that the SiO_2 surface caused the thixotropic thinning behavior of the filter cake.

A tentative explanation for the thixotropic thinning behavior is as follows. Si has an electronegativity of 1.90, which is higher than that of Al of 1.61, and hydrogen bonds easily form between Si–O–H groups. That is, hydrogen bonds form easily between particles that have Si–O–H groups on the surface in an aqueous environment. These lead to the formation of a network structure in which water is entrapped. This results in a filter cake with a high viscosity and seems dry. The network structure is easily destroyed by the action of a slight shear or disturbance, which causes the occluded water in it to flow out from the network to make a slurry. The viscosity of the slurry is very much smaller. This explanation is in agreement with previous works in the literature^{19–21} that reported that a thixotropic thinning behavior was exhibited when a three-dimensional structure developed between SiO_2 particles as a result of hydrogen bonding. The mechanism by which Si–O–H groups easily form hydrogen bonds needs to be further studied.

Furthermore, it was analyzed that three kinds of interactions acted on the particle surface, i.e., hydrogen bonding, van der Waals forces, and electrostatic repulsive forces. The hydrogen bond is a short-range force^{22,23} that disappears when the distance between particles is larger than the interaction range. The network structure, formed by hydrogen bonding, was rapidly destroyed once a shear or disturbance made the distance between particles larger than the interaction range. Also, the hydrogen bond has orientation due to the fixed angle of the O–H...O bond,^{24,25} which leads to the formation of a high void structure in the particles that would entrap more water in the structure. The experiments confirmed that the solid volume fraction of double layer coated cake (25.5%) was higher than that of the composite coated cake (20.9%). van der Waals forces and electrostatic repulsive forces are long-range forces, and they both vary linearly with the reciprocal of the square of the distance. They decrease gradually with the distance between particles, so the aggregates that are formed by these two forces are weakened only gradually when the distance between particles is increased due to a shear increase. Also, van der Waals forces and electrostatic repulsive forces do not have orientation, so the aggregates are more compact and have a high solid volume fraction.

Therefore, for particles with Si–O–H groups on their surface, hydrogen bonding has a dominant role in the interaction of the particles. The structure formed between the particles entraps more water, but once a shear or disturbance acts on the structure, it is easily destroyed and the entrapped water flows out. Their cakes would show thixotropic thinning behavior. For particles with Al–O–H groups on their surface, van der Waals forces and electrostatic repulsive forces dominate the interaction of the particles. When a shear or disturbance acts on the cake, its viscosity changes only gradually with the shear rate, and it shows a shear thinning behavior. For the composite coated particles, there were both Si–O–H and Al–O–H groups on the coated aluminosilicate surface, and the Si–O–H groups cause the formation of a network structure of particles through hydrogen bonds, leading to the thixotropic thinning behavior of the filter cake.

4. CONCLUSION

A filter cake made of TiO₂ particles coated with a SiO₂–Al₂O₃ composite layer showed a thixotropic thinning behavior, while a filter cake made of TiO₂ particles with a SiO₂–Al₂O₃ double layer coat showed a shear thinning behavior. It was the difference in the coating surface, whether it had Si–O–H or Al–O–H groups, that caused this difference in cake rheology. A possible reason is that particles with Si–O–H groups on their surface easily formed a network structure by hydrogen bonding. This structure entrapped water but was easily destroyed by a shear or disturbance, causing the occluded water to flow out to form a slurry. The viscosity of the resulting slurry was very much smaller. By putting a thin layer of Al₂O₃ coating on the SiO₂–Al₂O₃ composite coated particles, the thixotropic thinning behavior was eliminated and the cake rheology became similar to that of the filter cake made from SiO₂–Al₂O₃ double layer coated particles.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-10-62788993. Fax: +86-10-62772051. E-mail: wangtj@tsinghua.edu.cn.

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