

Computer simulation on titania particle agglomeration

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티타니아 입자의 응집에 대한 컴퓨터 시뮬레이션

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Abstract The agglomeration of titania particles with 30 nm in radii was simulated based on the colloidal stability. For surface potential increase from 4.5 to 16.8 mV, the height of energy barrier increased. This tendency may explain the experimentally observed aggregation behavior where particles with smaller size and higher potential exhibited higher stability but form bigger and harder agglomerates with irregular shapes after drying.

요 약 30 nm의 입자반경을 가지는 티타니아 입자의 응집을 콜로이드 안정성에 기초하여 컴퓨터 시뮬레이션하였다. 제타 포텐셜이 4.5에서 16.8 mV로 증가할 때 에너지 장벽이 높아진다. 이러한 경향은 실험에서 입자크기가 작을수록 포텐셜이 높을수록 입자가 응집이 적어지는 안정한 상태가 되어 건조시에 불규칙한 형상과 강한 입자간 결합을 형성한다는 실험실적 관찰 결과와 일치한다.

1. Introduction

Titania powder processing has been studied because of its wide commercial applications. Many research results on the synthesis of spherical titania powder have been reported [1-9]. Homogeneous precipitation was applied to obtain the controlled shape and morphology of titania powder. The morphology of powder was known to be affected by the starting materials, solvent, concentrations, reaction temperature and reaction time, etc.

Uniform titania powder with spherical morphology was synthesized by aging titanium tetrachloride at 97°C by Matijevec *et al.* [1] The morphology of powders was affected by the concentrations of Na₂SO₄ used as an additive to regulate the precipitation in their report. Spherical titania was obtained using alcoholic solutions of titanium alkoxides by Barringer and Bowen [2], although their process was found to have no reproducibility [3]. There have been reports illustrating the important role of interparticle potential in

colloidal particles on the morphology of aggregates. Look and Zukoski [3-6] studied the effect of interparticle potential on the morphology of particles in the homogeneous precipitation process and found that colloidal stability is necessary for precipitation of narrow size distribution of titania powders formed in aqueous ethanol. Effect of solvent on the precipitation of titania powders was studied by Harris and Byers [7] during homogeneous precipitation using an alcoholic aqueous solution of titanium ethoxide. Park *et al.* [8, 9] synthesized titania powders through the thermal hydrolysis of titanium tetrachloride and titanium sulfate in a mixed solvent of n-propyl alcohol and water.

General approaches have been trial and error method even though there have been much progress to get optimum processing condition. This research has been intended to simulate titania powder agglomeration based on the reported interparticle potential energy [3-5] in order to observe the effect of major variables like surface potential and the dielectric constant of solvent in the agglomeration process. We were

trying to simplify the agglomeration process by considering just one agglomerate in the suspension and to correlate the processing variables with the final properties of titania powder product.

2. Modeling

A particles potential energy is assumed to be the simple sum of its interactions with all other particles [10-13]. We assumed that there are three contributions to the interparticle potential energy, van der Waals attractive (VWA), electrostatic repulsive energy (ER) and short range repulsion (SRR) [3-5, 9]. Hamaker derived van der Waals attractive energy equation on the basis of additivity of the energies between pairs of atoms or molecules. In the case of the attraction between two particles of radius, a , at a distance, r , between two surfaces Hamaker's equation is as follows,

$$V_a(r) = \left(-\frac{2}{4 - \left(\frac{r}{a}\right)^2} + 2\left(\frac{a}{r}\right)^2 + \ln\left(\frac{\left(\frac{r}{a}\right)^2 - 4}{\left(\frac{r}{a}\right)^2}\right) \right) \times \left(-\frac{A}{6}\right) \quad (1)$$

where Hamakers constant, A depends on the properties of the particles and of the dispersion medium.

Electrostatic interaction energy causes repulsion between particles if they are of the same chemical nature and have surface field of the same sign and magnitude. This repulsion energy is due to the interaction of surface potential in the double layers and falls off as an exponential function of distance. The electrostatic repulsive energy's range is the thickness of the electrical double layer.

$$1/\kappa = \left(\frac{\epsilon\epsilon^0 RT}{F^2 \sum (c_i z_i^2)} \right)^{\frac{1}{2}} \quad (2)$$

where ϵ is the relative dielectric constant of the medium, ϵ_0 the dielectric constant of the vacuum, R the gas constant, T the absolute temperature, F the Faraday constant, c_i and z_i are the concentration and the charge of type i ions in the dispersion medium.

We used the Derjaguin approximation of electrostatic repulsive potential as follows.

$$V_e = 2\pi\epsilon\epsilon^0 a\phi^2 \ln\left(1 + \exp\left(\kappa a \left(2 - \left(\frac{r}{a}\right)\right)\right)\right) \quad (3)$$

where r is the interparticle distance between particle

centers.

For quantitative estimates of the effects of the short-range repulsive potential, we used the short range repulsive potential equation proposed by Look and Zukoski [3-5] as follows.

$$V_s = \pi S_a L_s a \exp\left(\left(\frac{a}{L_s}\right) \times \left(2 - \left(\frac{r}{a}\right)\right)\right) \quad (4)$$

where its form is estimated using a Derjaguin approximation for the exponentially decaying solvation force and S_a is a pre-exponential factor of $1.5 \times 10^3 \text{ J/m}^2$ and L_s is a characteristic decay length of 1 nm.

Parameters used are in appendix I. FORTRAN 90 source code is available on request. Typical potential energies of a titania colloidal particle in a suspension are shown in Fig. 1. Experimental conditions in titania powder agglomeration research done by Park *et al.* [8] were used as simulation conditions where titania powders were synthesized by thermal hydrolysis of titanium tetrachloride in a mixed solvent of *n*-propanol and water, where the morphology of the precipitates

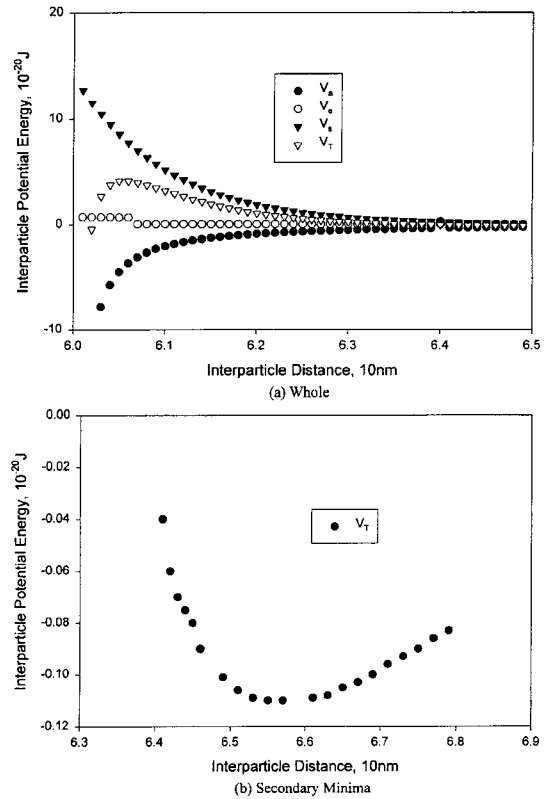


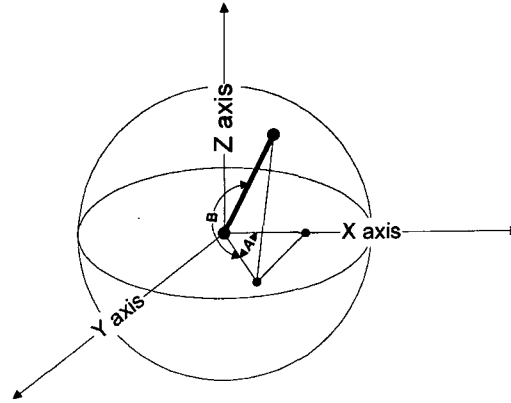
Fig. 1. Typical potential curve of a titania colloidal particle in a suspension with low potential (Dielectric Constant 32 and Zeta Potential 4.5 mV).

Table 1
Experimental Conditions for Three Samples [8]

| Name condition | Low potential | Middle potential | High potential |
|------------------------------|---------------|------------------|----------------|
| Relative dielectric constant | 32.0 | 32.8 | 80.4 |
| Zeta potential (mV) | 4.5 | 8.9 | 16.8 |

was controlled by adjusting the volume ratio of *n*-propanol to water (RH ratio) of the mixed solvent. They changed the zeta potentials of the precipitates and the dielectric constants of solvents and reported that the discrete particles obtained at the RH ratio 3, which resulted from the low zeta potential of the precipitate and the low dielectric constant of solvent. The zeta potential of the precipitates and the dielectric constant of the mixed solvent (with RH ratio of 3) was lowered due to the chemical adsorption of alcohol on the particle surface. We simulated the agglomeration process of titania particles and compared the experimental observations of three samples in Table 1 by Park *et al.*[8] with the simulated particle agglomerates, and discussed the simulation results later to check the effects of three variables (particle size, zeta potential, and dielectric constant).

In order to simulate the agglomeration of titania particles, an explicit finite difference method was designed. At the same time, in order to simplify the computation, one agglomerate approach was designed where one particle was generated as a seed at an arbitrary position; $X = 5$, $Y = 5$ and $Z = 5$ (micron), and other particles are added to the seed particle one by one from outside. In this simulation, mono-dispersed system was assumed and representative particle radius was 30 nm. All these processes were visualized on computer screen where computer screen was set to the size of 12 micron by 8.5 micron approximately. After generating seed in the center, another particle was generated far outside, in the distance of 2.5 micron from the center of seed, with angles randomly selected as shown in Fig. 2, where two angles are necessary to define the coordinates of particles in three dimension. Total interparticle potential energy between a new particle in the space and the seed particle was calculated using equation (1), (2), and (4) by summing three equations. These calculations were repeated by moving the new particle into the center of the seed particle 1000 times in a step of 0.0025 micron or 2.5 nm, where these conditions were selected by pre-study. Figure 1(a) shows one of the typical potential curves of a titania colloidal particle in a suspension



$$X = 2.5 \text{ micron } \cos(B) \cos(A) + 5.0$$

$$Y = 2.5 \text{ micron } \cos(B) \sin(A) + 5.0$$

$$Z = 2.5 \text{ micron } \sin(B) + 5.0$$

Fig. 2. Schematic representation of particle generation in the distance of 2.5 micron with angles, A and B, randomly selected.

with dielectric constant 32.0 and zeta potential 4.5 mV, where zeta potential value was used as a surface potential value and this substitution is usual in the calculation of colloidal stability. Figure 1(b) shows one part of Fig. 1(a) near the secondary minimum, which is typical to titania colloidal particle in a suspension. Energy barrier in Fig. 1(a) prevents the agglomeration of titania particles unless particles have high kinetic energies enough to overcome this energy barrier.

After calculating the distribution of interparticle potentials along the line between the new particle and the seed, the new particle was allowed to move toward as far as there was no energy increase where the unit step of particle is 2.5 nm as mentioned above. The unit step is important to find the minimum energy position and the computation time at the same time. If the unit step is too big, the minimum position found here is far from the true minimum energy. If too small, it takes too long time to reach the minimum energy position in a reasonable computation time. This process is repeated for one thousand particles generated in a 2.5 micron sphere around the seed position at the center (5, 5, 5 (micron)) in monitor size about 12×8 (micron). Particles were assumed to be agglomerated one by one according to the collective interparticle potential and all these agglomeration processes were programmed by personal computer. After generating the target agglomerate, the radial distribution of particles around the seed particle was used to analyze

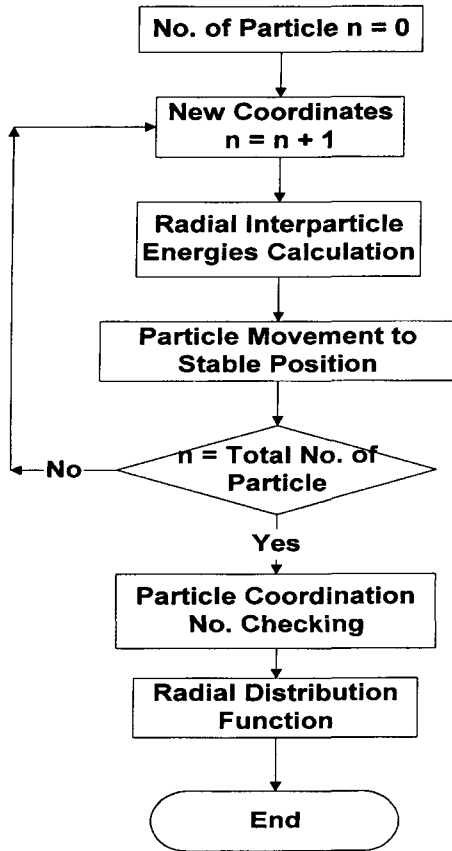


Fig. 3. Flowchart of particle agglomeration process.

the microstructure of agglomerate, which was compared with experimental findings later. All the coordination numbers of all the particles in the agglomerate were checked and discussed later for the same purpose. All these processes are summarized in Fig. 3.

3. Discussion

Figure 1(a) shows three potential curves, attractive energy V_a , electrostatic repulsive energy V_e , short range repulsive energy V_s , and the total potential energy curves of a titania colloidal particle in a suspension with dielectric constant 32.0 and zeta potential 4.5 mV. Total potential curve shows the first minimum near the particle contact point and the total potential increases as the interparticle distance increases. This potential increase induces an energy barrier, which prevents direct particle contact. Figure 1(b) shows the same total potential energy curves magnified around the secondary minimum located in the far side of the

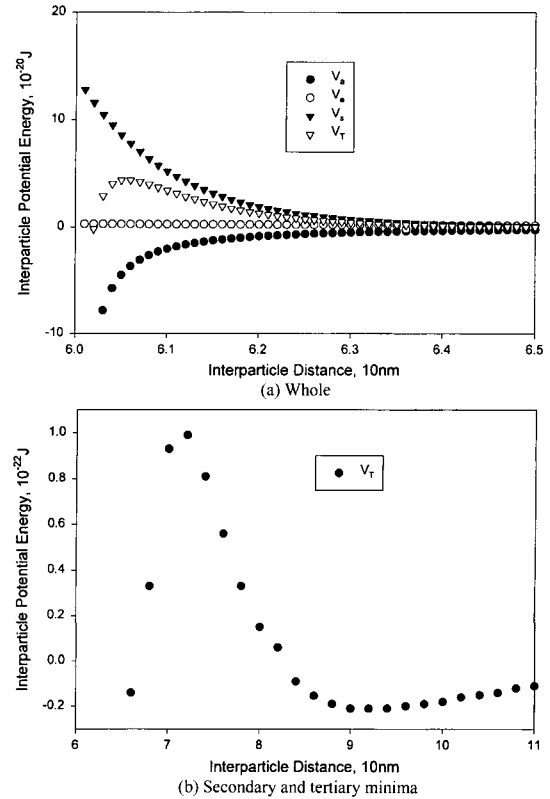


Fig. 4. Typical potential curve of a titania colloidal particle in a suspension with middle potential (Dielectric Constant 32.80 and Zeta Potential 8.9).

energy barrier from the first minimum. In Fig. 1(b), secondary minimum is found to be around 65 nm, where particles are assumed to reside in a suspension with dielectric constant 32.0 and zeta potential 4.5 mV. On the other hand, Fig. 4(a) shows similar potential curves of a titania colloidal particle in a suspension with higher dielectric constant 32.80 and zeta potential 8.9 mV. In Fig. 4(b), secondary minimum is found to be around 67 nm, which is quite close to the interparticle distance found in Fig. 1(b) but in addition to the secondary minimum, tertiary minimum is found to be around 90 nm. This difference in the potential curves would affect the agglomeration behavior of titania particles. At high dielectric constant and zeta potential, the total potential curves of a titania colloidal particle increased at all interparticle distances as shown in Fig. 5 (in a suspension with dielectric constant 80.4 and zeta potential 16.8 mV). Secondary minimum in this curve is not clear but it shows nearly constant value after 150 nm and the secondary minimum is found to be around 180 nm. This secondary minimum is far big-

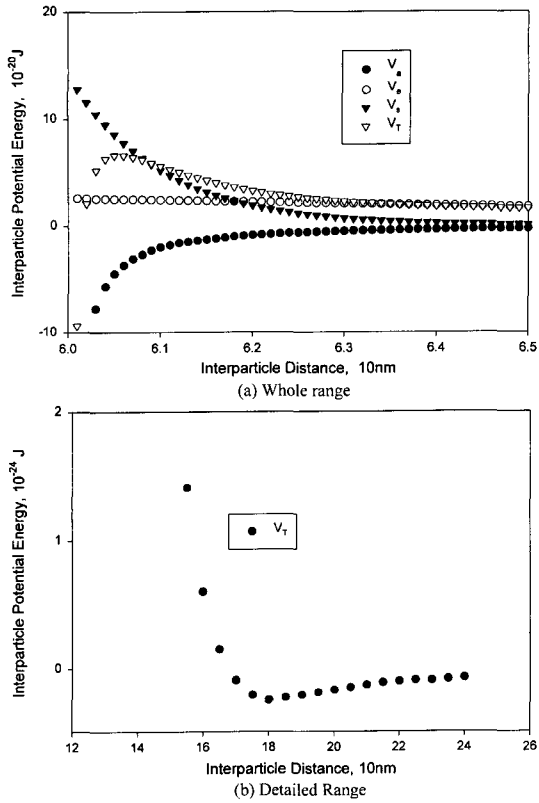
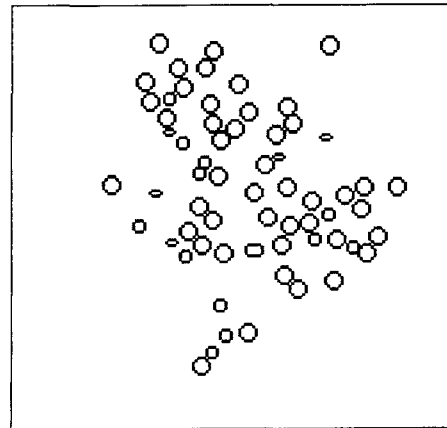


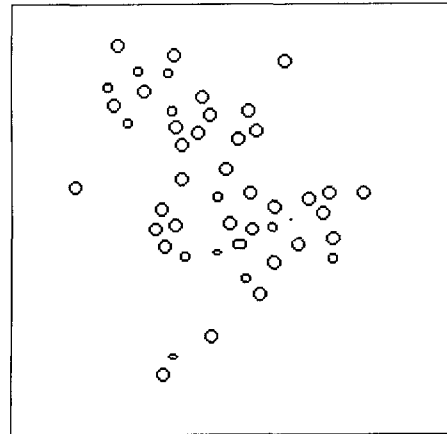
Fig. 5. Typical potential curve of a titania colloidal particle in suspension with high potential (Dielectric Constant 80.4 and Zeta Potential 16.8).

ger than the secondary minima observed in Fig. 3(b) and Fig. 4(b).

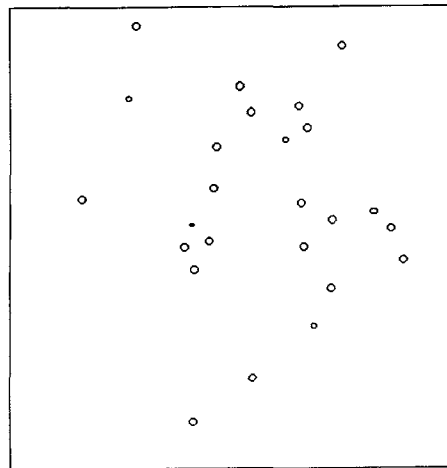
Figure 6 shows the cross-sections of simulated agglomerates in three different conditions, which were screen-captured on computer directly after simulation. Figure 6(a), (b), and (c) show the cross-section of a titania colloidal agglomerate in a suspension with dielectric constant 32.0 and zeta potential 4.5 mV, with dielectric constant 32.80 and zeta potential 8.9 mV, and with dielectric constant 80.4 and zeta potential 16.8 mV, respectively. Figure 6(a), (b), and (c) show gradual changes in the agglomeration from the agglomerated state in Fig. 6(a), in a suspension with low dielectric constant 32.0 and zeta potential 4.5 mV, to the dispersed state in Fig. 6(c), in a suspension with high dielectric constant 80.4 and zeta potential 16.8 mV. Especially, tertiary minimum is found around 90 nm in Fig. 6(b), which should overcome in order to approach the secondary minimum. These agglomerates show different particle packing structure strongly affected by the interparticle potential, which agrees well with the



(a) dielectric constant 32.0 and zeta potential 4.5mV.



(b) dielectric constant 32.80 and zeta potential 8.9.



(c) dielectric constant 80.4 and zeta potential 16.8.

Fig. 6. Cross-section of simulated agglomerates in three different conditions.

experimental results by Look and Zukoski [3-6].

This trend in Fig. 6 is checked with the radial distri-

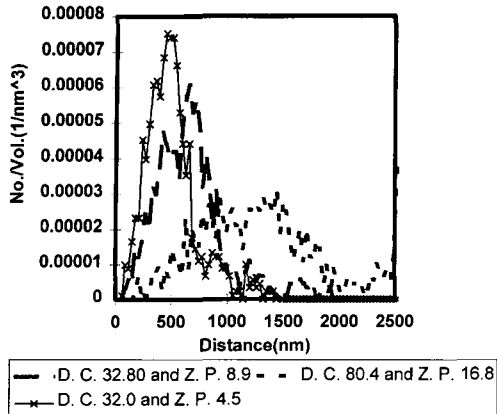


Fig. 7. Radial distribution of particles at three different conditions.

bution of particles at three different conditions in Fig. 7, where Fig. 7 shows gradual changes in the packing microstructure from the compact state showing population maximum at about 500 nm, in a suspension with low dielectric constant 32.0 and zeta potential 4.5 mV, to the loose state showing population maximum at about 1500 nm, in a suspension with high dielectric constant 80.4 and zeta potential 16.8 mV. This trend from the compact state to the loose state quite agrees well with the observations in Fig. 6. The population maximum changed from 500 nm in the compact state to 1500 nm in the loose state, which is three times bigger than the population maximum in the compact state. This difference in the population maximum implies the difference in the particle packing structure, where the loose structure occupies much bigger (about 27 times) space than the compact state. In order to con-

firm this trend, particle coordination number was checked. Figure 8 shows the coordination numbers of particles within the distance of particle diameter from the surface of each particle at the same three different conditions in Fig. 7. The coordination numbers of all particles were linearly regressed with the number of particles because of big fluctuations in data. Regressed lines in Fig. 8 show gradual changes in the coordination number showing the distribution of 10 to 5, in a suspension with low dielectric constant 32.0 and zeta potential 4.5 mV, to almost zero in a suspension with high dielectric constant 80.4 and zeta potential 16.8 mV. As a result, regression analysis on three curves shows that coordination number is decreasing fast in the smallest agglomerate in the suspension with low dielectric constant 32.0 and zeta potential 4.5 mV but decreasing little in the largest agglomerate in the suspension with high dielectric constant 80.4 and zeta potential 16.8 mV. These trends show quite similar agglomeration process with the schematics of particle growth in the mixed solvent of alcohol and water [8].

As a conclusion, suspension with low dielectric constant and zeta potential shows strong agglomeration to make stable agglomerates and agglomeration increases the repulsive energy barrier at the same time. These powders with low dielectric constant and zeta potential form strong small agglomerate and maintain this state even during drying process to generate uniform powders with narrow size distribution because they already form agglomerates in the suspension. On the other hand, suspension with high dielectric constant and zeta potential shows big energy barrier to prevent particle agglomeration and stable in colloidal state. These stable colloidal particles become unstable due to their surface energies during drying stage because they did not form stable agglomerates in the suspension. Loose agglomerate form stable agglomerate suddenly during drying process to generate powders with bigger size distribution due to the rapidness of the agglomeration process [8, 9].

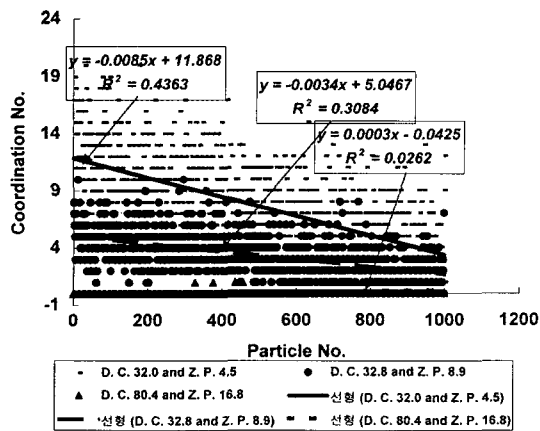


Fig. 8. Coordination number of particles and linear regression lines at three different conditions.

4. Conclusions

A new method for the simulation of the agglomeration behavior of titania particles using collective potential energy concept has been presented. The prediction of agglomeration behavior from this simulation agrees well with the experimentally observed phenomena and provides fundamental understanding on the formation

of agglomerates from colloidal titania particles. Three different suspensions with different dielectric constant and zeta potential have been simulated and compared with the experimental observations. Simulated agglomerate microstructure shows good similarity with the experimental observation and provides useful information on agglomerate microstructure.

Suspension with low dielectric constant and zeta potential shows strong agglomeration to make stable agglomerates and to maintain its shape even during drying process to generate uniform powders with narrow size distribution. Suspension with high dielectric constant and zeta potential shows big energy barrier to prevent particle agglomeration and agglomerate suddenly during drying process to generate powders with bigger size distribution.

Appendix I. Parameters used in potential energy calculation.

$$A = 2.5 \text{ kT (at room temperature } 25^\circ\text{C)}$$

$$\varepsilon^0 = (36\pi)^{-1} \times 10^{-9} = 8.854 \times 10^{-12} \text{ F/m}$$

$$\varepsilon = 32.0, 32.8, 80.37$$

$$a = 0.03 \text{ } \mu\text{m}$$

$$\phi_0 = 4.5 \text{ mV}, 8.9 \text{ mV}, 16.8 \text{ mV}$$

$$1/\kappa = (\varepsilon\varepsilon^0RT/F^2 \sum_i c_i z_i^2)^{1/2}$$

$$R = 8.314 \text{ J/mole } ^\circ\text{K}$$

$$F = 96500 \text{ coul/equiv.}$$

$$c_i = 0.24 \text{ mol m}^{-3}$$

$$z_i = 2 \text{ equiv/mole (monovalent ion)}$$

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