Original Research Paper

Electrical-driven disaggregation of the two-dimensional assembly of colloidal polymer particles under pulse DC charging

M. Nazli Naim [a], Motoyuki Iijima [a,b,c], Keitaro Sasaki [a], Masahiko Kuwata [d], Hidehiro Kamiya [a,b,c], I. Wuled Lenggoro [a,b,c,*]

[a] Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Naka Cho, 2-24-16, Koganei, Tokyo 184-8588, Japan
[b] Department Chemical of Engineering, Tokyo University of Agriculture and Technology, Naka Cho, 2-24-16, Koganei, Tokyo 184-8588, Japan
[c] Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Naka Cho, 2-24-16, Koganei, Tokyo 184-8588, Japan
[d] Department of Environmental Engineering for Symbiosis, Soka University, 1-236, Tangicho, Hachioji, Tokyo 192-8577, Japan

ARTICLE INFO

ABSTRACT

Two-dimensional structures of polymer (polystyrene) colloidal particles were formed on a substrate by electrophoretic deposition in an aqueous suspension. The prepared suspension is stable for a few days; therefore, it was not necessary to place an additional mixing during the deposition process. The particle aggregation/disaggregation formation was observed on the metal surface in order to study the effect of pulse direct current (DC) charging in comparison with conventional DC charging. At the charging frequency of 80 Hz, it was observed that pulse DC charging with a maximum applied voltage of 3.3 V/cm (50% duty cycle) clearly reduced the degree of aggregation of particles having diameters of 50 and 300 nm comparing to those of DC charging. Pulse charging at high frequency is thus found to be more effective in preventing particle aggregation during electrophoretic deposition than conventional DC charging.

© 2010 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan. All rights reserved.

1. Introduction

Movements of colloidal particles in solvents and their electrokinetics were known since early 19th century, but extensive studies have recently been made for various kinds of application [1–4]. Coating of nanoparticles on various kinds of surfaces (e.g., electrophoretic deposition, EPD) is one of the fields of wide interest. EPD is generally defined as the motion of charged particles in a suspension under the influence of an electric field. The process includes deposition of charged particles onto a substrate surface with an opposite charge. Though various materials have been explored by this technique [5,6], difficulties in preventing nanometer-sized particles from aggregation during deposition remain unsolved [7–9]. Disaggregation, or single (individual) particle deposit become very important when the functions or performance of particles per area is highly demanded in such applications of metallic nano-particles as in sensors, catalyst or sterile surfaces. For example, it is reported that silver particles of less than only 1 ppm/μm^2 are required to incapacitate 99.9% of bacterial population by bind-ing their protein molecules, causing inhibition of cellular metabolism to death [10]. When the amount of required particle is low, an appropriate particle number per area is required to optimize surface utilization.

The purpose of the present study is to utilize mono-dispersed polystyrene latex (PSL) particles as model particles per area as they are deposited from an aqueous suspension. Instead of single-size particles, a wider particles size distribution (binary particles) is also included in order to evaluate the effect of size distribution on the structure of deposit particles. The particles were deposited by pulse direct current (DC) EPD to take advantage of the charging method for producing the structure of particles with a controlled degree of aggregation. This technique has achieved formation of two-dimensional particle layers with an exact amount of suspended particles deposited onto a stainless steel surface, as confirmed by observation of the morphology of particle aggregation under the influence of charging methods.

2. Experiment method

2.1. Preparation of colloidal particles

Three different kinds of as-received polystyrene latex particles (Duke Scientific Cooperation, USA) were used after dilution. Each

* Corresponding author. Address: Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Naka Cho, 2-24-16, Koganei, Tokyo 184-8588, Japan.
E-mail address: wuled@cc.tuat.ac.jp (I.W. Lenggoro).

of the suspension was diluted with ultrapure water (Milipore Co. Ltd) until the particle concentration number reached a preset pH value, between 6.3 and 6.4. According to the maker, each latex particle had one of the three nominal diameter sizes: 50 nm (1 wt%), 100 nm (1 wt%) and 300 nm (10 wt%). By assuming the particle density, $\rho_p = 1.05$ kg/m^3, the particle number was estimated as follows:

$$N_{psl} = \frac{M_{total}}{M_{PSL}} \tag{1}$$

where M_{total} is the total initial mass of the as-received particles, M_{PSL} is the mass of one PSL particle, defined as

$$M_{PSL} = \pi/6 D_p^3 \rho_p \tag{2}$$

and D_p is the particle diameter. In order to imitate the actual particle behavior upon the pulse DC charged EPD process, each of the prepared media should be deposited with approximately the same particle concentration number, time and applied voltage. For comparison purpose, a sample with the same operation condition was also prepared and deposited by the conventional DC charging. Prior to the deposition process, the suspension was sonicated for 5 min to avoid fouling on the wall of bath surface. The particle size distribution was measured by a dynamic light scattering (DLS) analysis (Malvern Instrument, HPPS 5001). The zeta potential was measured by a Zeta Potential Measurement Apparatus (Nihon Rufuto Co. Ltd., model 502) to determine the surface charge condition on the surface of the suspended particles.

In order to reproduce the previously prepared single-size particle suspension, mixtures of binary (50 and 300 nm) particles were prepared together in the same media. The operation condition of the mixture was the same as that of the single-size particle. Prior to the EPD process, the particle size distribution of each medium was re-measured by DLS to ensure that the mixture particles were not aggregated during the preparation process.

A stainless steel wire (SUS316) with 250 μm diameter and 25 mm length was used as a substrate, which was placed as an anode and treated in a pretreatment stage. The substrate in this stage was pretreated and sonicated with sulfuric acid (0.1 M) at 50 °C for 10 min, rinsed with water for 5 min, and finally sonicated in acetone for 2 min. A platinum plate with a dimension of $50 \times 15 \times 0.5$ mm^3 was used as a counter electrode (cathode).

2.2. Particle deposition

Each electrode was submerged into the prepared media with a 3 cm distance at 26 ± 2 °C. A pH probe was placed in the bath to monitor the pH value before and after deposition. Electrophoretic deposition (EPD) with DC voltage up to 3.3 V/cm was applied during the deposition. An in-house built circuit, calibrated with a digital electrometer (Keithley Instrument Inc., Type 617) and an oscilloscope (Textronix Inc., TDS 2002B), were used to control the pulse current and to measure the current density. The frequency of each pulse cycle was fixed at 80 Hz and was kept constant for each bath. A data logger (Graphtec Corp., GL200) was used to record the average current density from the anode. Pulse time intervals or frequencies were controlled by a field-effect transistor (FET) and were assisted by an optical coupler. The design circuit has been fixed to 50% duty cycle that made the value of one 1 min in DC will equal to 2 min in pulse DC. These combinations between the working electrophoretic bath and the circuit enabled us to determine the actual time and altitude of each pulse during the deposition. The setup of the whole apparatus was similar to our previous work [11].

The net charging periods during the deposition process of pulse DC and DC was controlled to be 2 min for each process. The deposited substrate was heated to 60 °C for 5 h in a furnace to evaporate the remaining water. Mixture particles were charged similarly (equal charging voltage and frequency, etc.) to that in our previous study with single-size particles. However, the charging time was varied from 5 to 30 min for comparison with the results on single-size deposit particles. Conventional DC charging was also conducted for comparison.

2.3. Characterization

The morphology of dried deposit particles was characterized using field emission scanning electron microscopy (FE-SEM) (JEOL Tokyo, JSM 6335F). The state of aggregation was determined by an imaging-processing program, Win Roof (Mitani Corp.). During the analysis, each particle was automatically marked to avoid incorrect boundary determination of the structure. In this study, a single (individual) particle is defined as a primary particle available in the suspension that had successfully deposited on the surface of stainless steel. Duplet, triplet or higher-order species are defined as aggregate deposited structure build by individual particle during the EPD process.

3. Results and discussion

3.1. Structure from single-size particle

Single-size particles are deposited to model the particle structures under the effect of different charging modes. Since the number of particles per volume is fixed, two-dimensional deposits can be formed to study the effect of pulse charging onto a desired substrate. Fig. 1 shows the SEM images of different particle deposits formed by pulse DC charging at 50% duty cycle (Fig. 1(a), (c), (e)) and conventional DC charging (Fig. 1(b), (d), (f)) at 3.3 V/cm and 2 min. Both charging methods show that the number of particles per area slightly decreases with larger particle size. Deposition by pulse DC show low tendency of particle aggregation compare to conventional DC charging. The aggregation number increase when larger particle sizes are conducted. A quantitative analysis of the obtained image is shown in Fig. 2.

Fig. 2(a) shows the amount of particle deposits at pulse DC charging. The figure shows that both individual and aggregated particles were produced in this process. As shown, individual deposit particles decrease while aggregate deposit particles increase as the particle size increases from 50 to 300 nm. This behavior may be ascribed to the electrokinetic phenomena that happened on the surface of the substrate or reduction of the zeta potential [12,13,17]. When an electrophoretic or electrophoresis deposition occurred, two common phenomena are expected to cause the particle movement. These phenomena can be expressed as electrophoresis and electroosmosis, and commonly referred to as electrokinetic phenomena. The details of these phenomena and their relation to particle movement during the charging will be discussed later with reference to Fig. 3.

The zeta potential, ζ, can be defined as the potential difference between the dispersion medium and the stationary layer of the fluid attached to the dispersed particles. The zeta potential is one of the important factors for determining the amount of deposit particles on a substrate according to Eq. (3) [12].

$$Y = \frac{lV\zeta\varepsilon c_s t}{3\ln(a/b)\eta} \tag{3}$$

Where Y is defined as the number of deposit particles or particle concentrations, l is the electrode length, V is the potential difference, ε is the permittivity, c_s is the particle concentration, t is the deposition time, and η is the medium viscosity, while a and b are

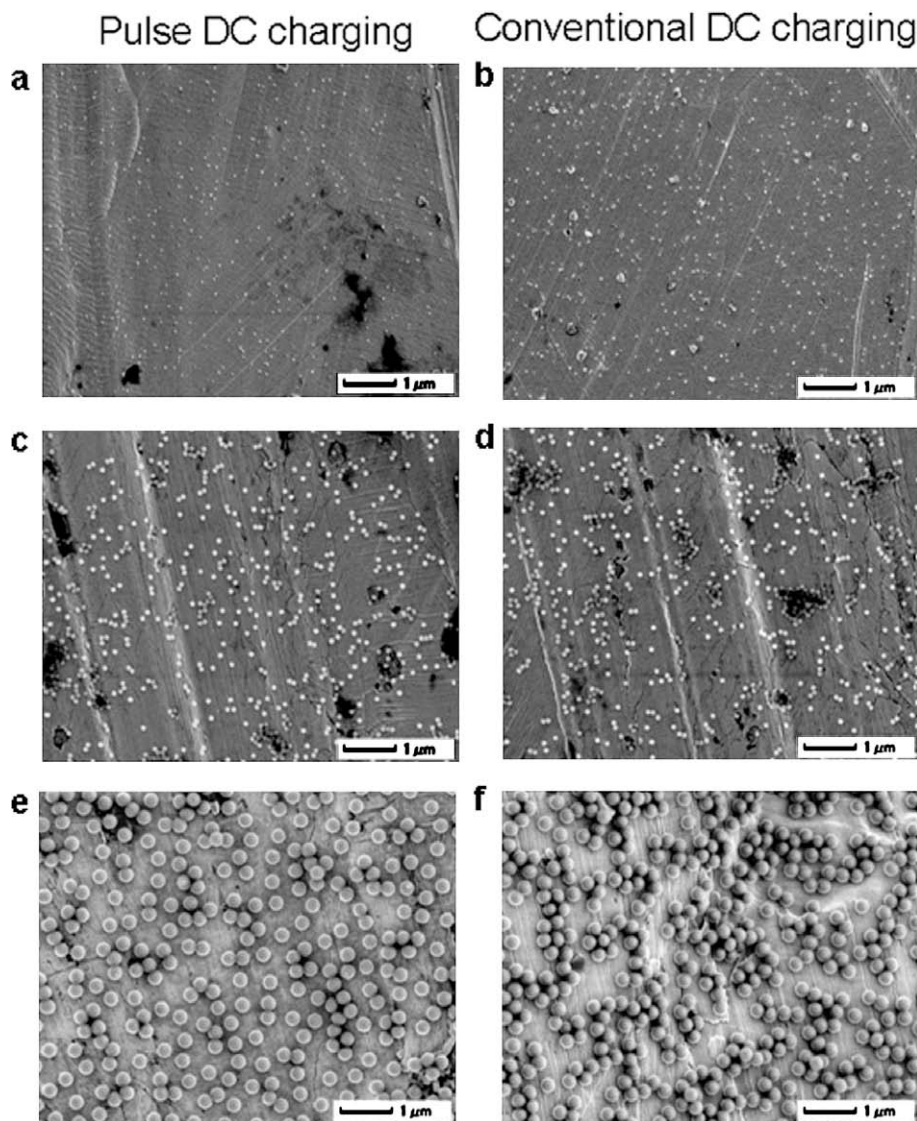Pulse DC charging   Conventional DC charging

Fig. 1. Single-size deposit particles by pulse DC charging and conventional DC charging. All particles are deposited at 3.3 V/cm and 2 min. Pulse DC charging was conducted at 80 Hz.

the cathode and anode diameters, respectively. In this study, the zeta potential value of each prepared particle sample is −26.3 mV (50 nm), −32.1 mV (100 nm) and −27 mV (300 nm). The pH value of the media as they are diluted in ultrapure water is between 6.3 and 6.4.

Fig. 2(b) shows the particle concentrations per area as conventional DC charging is conducted. It shows high decreasing and increasing rates of individual particles and aggregate particles, respectively, compared with those in Fig. 2(a). The higher rates in conventional DC charging compared to pulse DC charging show that an extra force influences the ordinary EPD process. This difference is probably related with the electrokinetic phenomenon, which has been mentioned above. It is also predicted that the electroosmosis force is higher in conventional DC charging compared to pulse DC charging. In both figures, the values derived from Eq. (3) are plotted for comparison. It is found that the calculated value does not exactly follow the experimental value on both figures. The difference between the calculated value and the experimental ones is might due to no electrokinetic influence that is suppose to be included during the calculation. The equation also only considers the transport phenomena near the substrate vicinity but neglecting the

increase of electro field resistant due to gas formation when long deposition time is applied.

The total number of deposit individual and aggregate particles in the case of 50 nm particles is found to be higher than that of 300 nm with pulse DC charging. This is related to the higher surface area of 50 nm compared to the 300 nm particles. For 50 nm particles, the difference of zeta potential value before and after the charging process is higher compare to that of 300 nm particles. The difference of zeta potential value also shows that undeposited particles have been exposed with a different pH value or ion concentration compare to the initial state. The difference on pH value or ion concentration occurs due to reduction and oxidation process at the electrode surface. High value of zeta potential difference shows that the particles are easy to be attracted to electrode surface and influenced by the electroosmosis phenomena. The details on this result will be further discussed in Fig. 8. With conventional DC charging, the difference is larger than the pulse DC charging, since the continuous electric potential induces the growth and the electroosmosis force higher than that of pulse DC charging.

In our hypothesis, the electrokinetic phenomenon near the substrate surface can be described as illustrated in Fig. 3. Within the
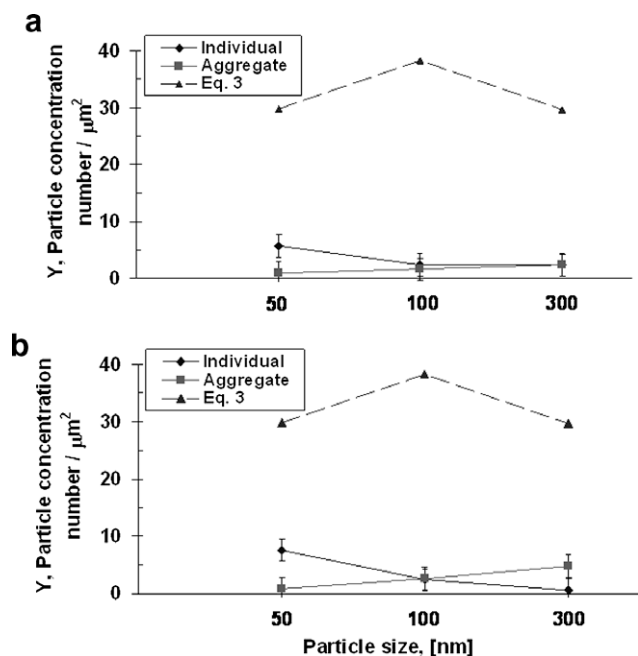
Fig. 2. Effect of charging voltage on the number concentration of particles by (a) pulse DC and (b) DC charging. The difference between pulse DC charging and DC charging obtained from previous SEM images. The results of calculation based on Eq. (3) are also plotted.

Debye length of the substrate surface, all nearby particles are easily influenced by electrokinetics. When an electrical field is applied, all particles are attracted to the substrate surface (i.e., electrophoretics). Under this condition, the force trajectory angle is tangent to the substrate surface. As the particles approach the substrate surface, an electroosmosis force interferes within the Debye length range [9,16]. This force bends the initially electrophoretic force, and it drives the incoming particles more to nearby deposit parti-

cles; hence it causes aggregation if the electrical field is continued. If the pulse charging EPD is conducted, however, the electroosmosis force is stopped at the off-mode condition. Since no driving force exists at this point, the suspended particles gather near the substrate without deposition. When the second on-mode occurs, the nearby particles are attracted to the substrate by the electrophoresis force with less influence from the electroosmosis force. The gathered particles are influenced more easily by electrophoretic than by the electroosmosis force, because the velocity of electrophoretics is higher than that of electroosmosis [13–15]. This mechanism explains why the deposition of more single particles occurred when pulse charging is conducted.

3.2. Structures from binary particles: 50 and 300 nm

Mixture suspensions with different particle sizes were deposited by EPD to model the particle characterization for a specific material (i.e., polystyrene) but with different characteristics such as surface charges and particle sizes. Combinations of particles with diameters of 50 and 300 nm were mainly chosen in this study, because it shows the closest zeta potential value or surface charge condition compared to the 100 nm particle size. A mixture of two particles with a very large difference in the zeta potential value is not recommended, because it will bring a driving force for complex interaction such as charge neutralization and particle collision. In some cases, mixture particles can get easily aggregate due to their different zeta potential values [18,19].

Fig. 4 shows FE-SEM images of the deposit structures formed from a mixture of 50 and 300 nm particles under various frequency and charging types. The operation condition was similar to those of single-size particle deposition. The frequency of the pulse DC charging was varied from 80 to 5 Hz to verify the results obtained from single-size particles. It was observed that the number of aggregated particles in the deposit increased when lower frequency charging was applied.

Fig. 5 shows the results of a quantitative analysis of the binary particles under the under the influence of various frequency and
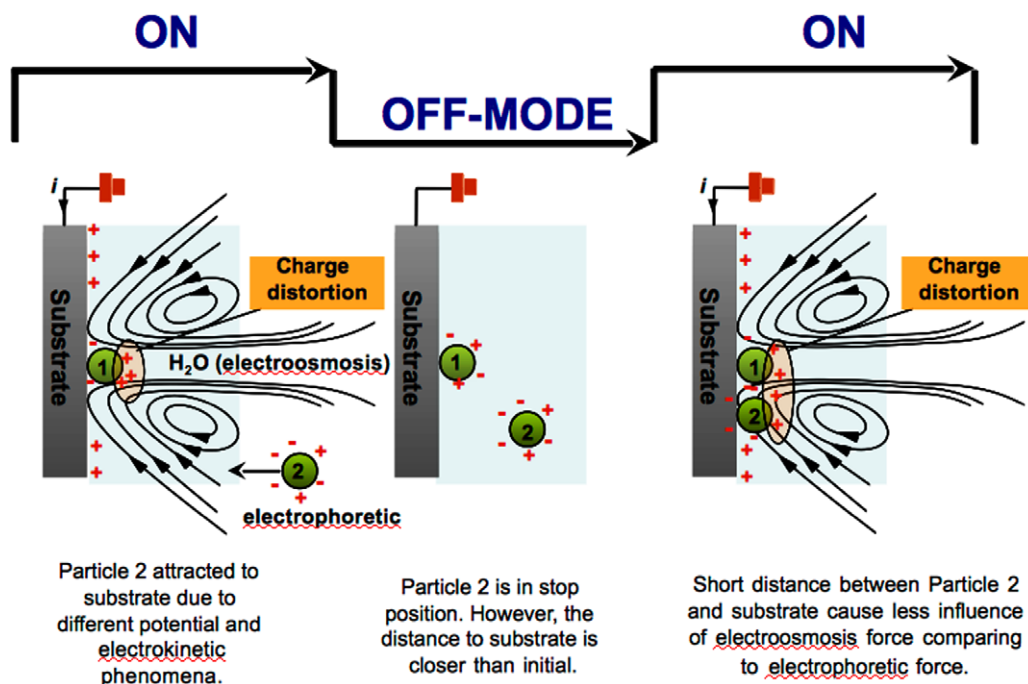

Fig. 3. Illustration of on-going deposit particles during EPD. The effect of electrokinetic phenomena is to induce the on-going particles as they approach the substrate. The off-mode condition reduces the effect of electroosmosis on an incoming deposit particle (particle 2).
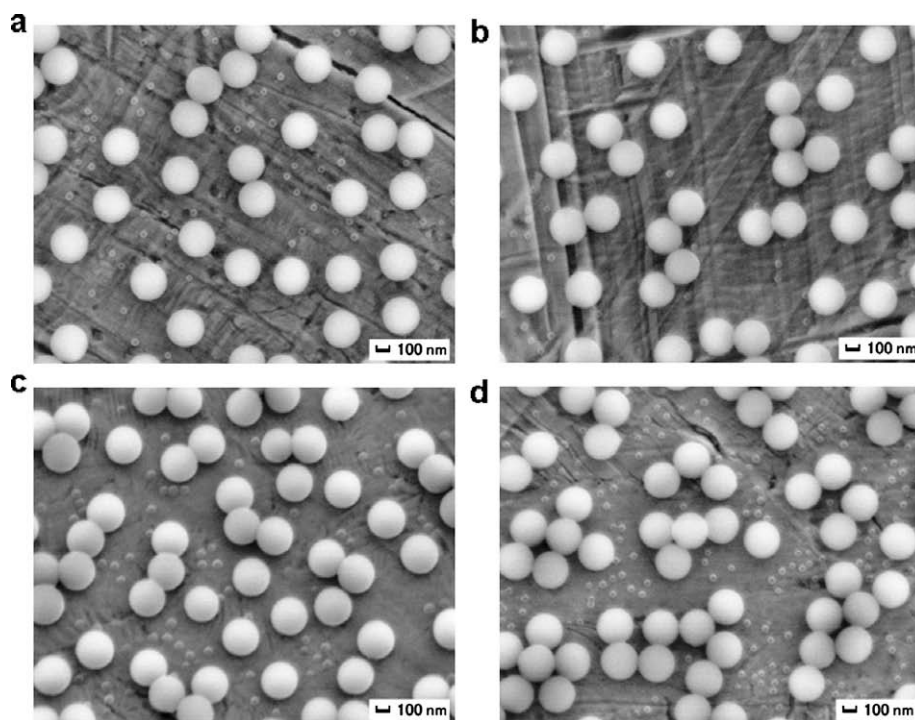
Fig. 4. Deposits of mixture particles (50 and 300 nm) by different charging conditions after heating (a) 80 Hz, (b) 40 Hz, (c) 5 Hz, and (d) DC. All particles are deposited at 3.3 V/cm and 2 min.

charging types. The results are obtained from the FE-SEM images. Fig. 5(a) are focusing on the 300 nm particles while Fig. 5(b) focusing on the 50 nm particles. When the pulse charging was allowed down, the number concentration of individual particle deposits
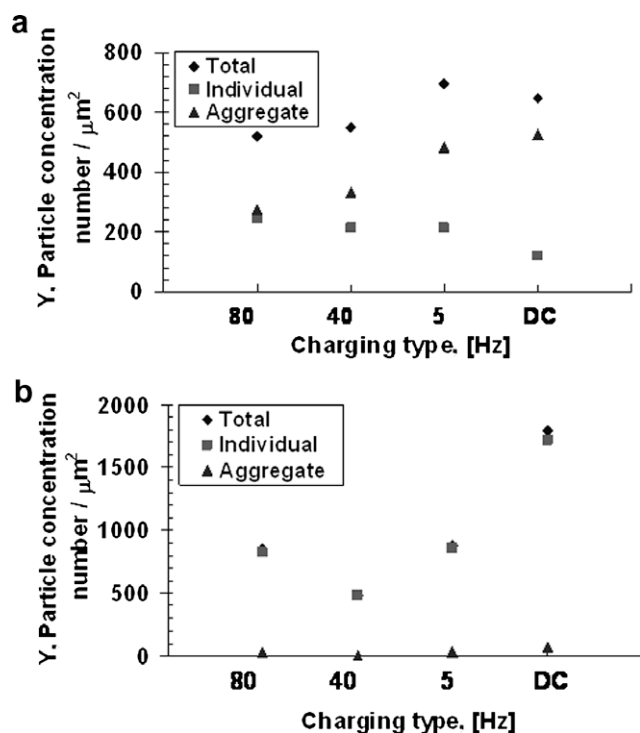

Fig. 5. Qualitative analysis of FE-SEM of deposit particles (a) 300 nm and (b) 50 nm. See Fig. 4 for charging conditions.

was reduced, as shown in Fig. 5(a), and minimized when DC charging was conducted. The number concentration of aggregated particles was increased almost simultaneously with the decrease in the individual particle deposit. Since the measurement of the number concentration of particle deposit is straightforward, we conclude that interference in the electroosmosis force becomes weaker than electrophoretic force as the charging frequency is increased.

Fig. 5(b) shows how the 50 nm particles interact with the surrounding particles as they were mixed and deposited together with the 300 nm particles. Since the condition was essentially identical to that for the EPD of single-size particles, the conditions of charging with 80 Hz pulse DC and DC should be unchanged. When low-frequency charging is applied, however, the deposit number of individual particles decreased slowly and then increased as 5 Hz and DC was conducted. This sudden increase in the number concentration of individual particle deposits might be due to the electroosmosis force that is strong enough to scatter the gathered 50 nm particles in the substrate vicinity. The scattered particles increase the particle Brownian motion. The increase in the particle Brownian motion causes each particle to deposit separately. As a result, the number concentration of individual particles decrease at 80 Hz and then increases at 40 Hz. The number concentration of the aggregated deposit particles seems to slightly increase as the charging with a lower frequency is applied. The different behavior of individual and aggregated particle deposits indicates that particles as small as 50 nm are hardly influenced by the electrokinetic forces. It is also indicated that 50 nm particles can be easily influenced by the electroosmosis force even at high frequency (i.e. when the electroosmosis force is small).

The FE-SEM images were also observed by varying the charging time, as shown in Fig. 6. In both figures, the charging time was fixed to 5, 10 and 30 min. As a comparison, conventional DC charging was also conducted. The 300 nm particles show mass aggregation (high-order aggregation) as DC charging was conducted (circle marks) while pulse DC charging did not show obvious mass aggregation.
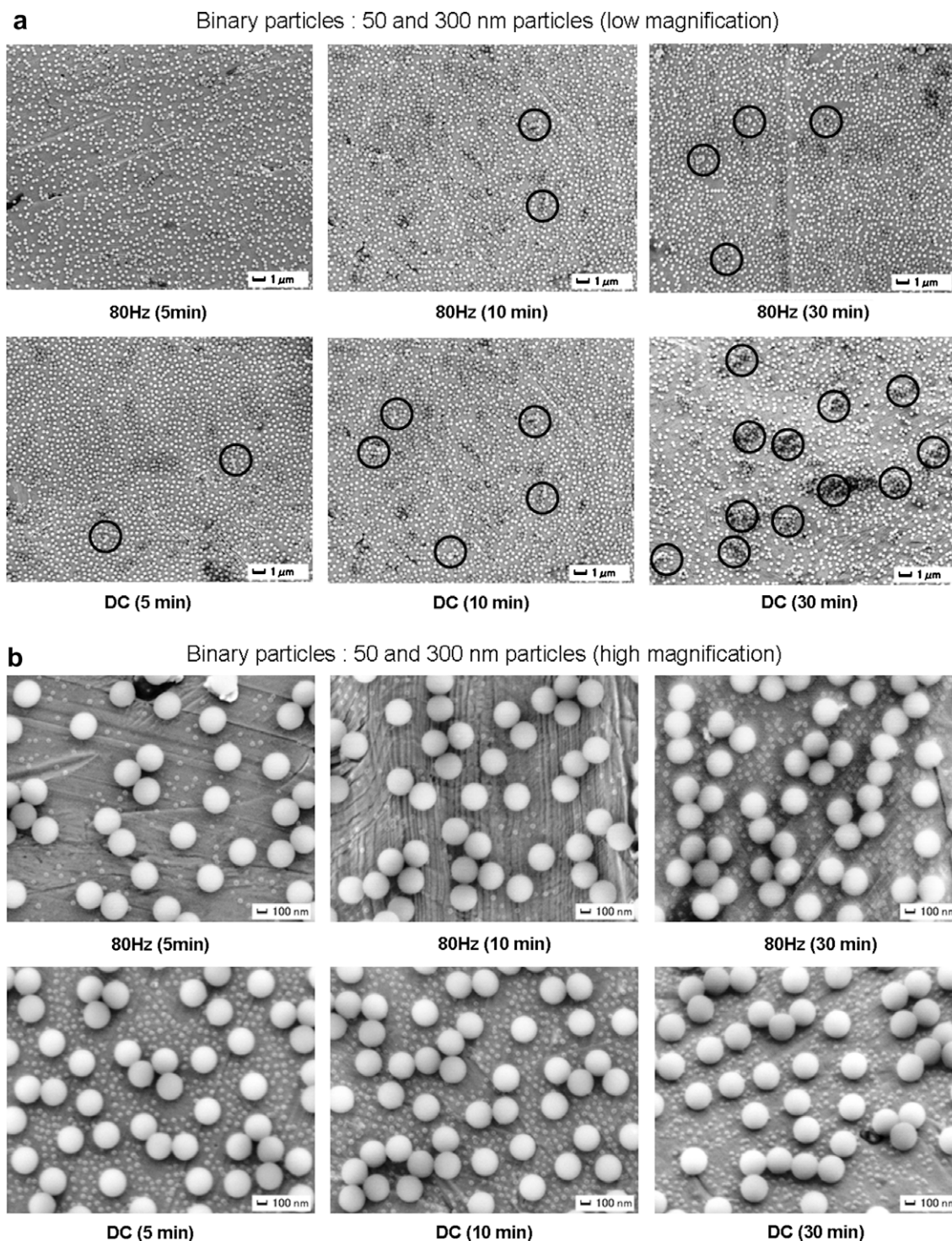
Fig. 6. FE-SEM of deposit of binary particles: 300 and 50 nm. Fig. 6(a) represents the low magnification of deposit structure while Fig. 6(b) represents high magnification of deposit structure. Charging time is varied from 5 to 30 min. Round marks represent higher-order aggregates.

The 50 nm particles in Fig. 6(b) do not show obvious mass aggregation; therefore, there is a good correlation between Fig. 6(b) and the data displayed in Fig. 5(b).

The comparison between the particles with different sizes shows that the 300 nm particle can be controlled more easily by the electrical charging (DC or pulse) than the 50 nm particle. This shows that the small electroosmosis force in pulse DC charging is strong enough to scatter the incoming 50 nm particles near the substrate instead of making them aggregate onto the deposit par-

ticles on the surface. In contrast, the larger incoming particles (300 nm) get easily aggregated depending on the charging frequency, because the electroosmosis force is high enough to overcome the electrophoretic force of the incoming particles.

3.3. Size distribution and surface charge of undeposited particles

A further analysis on the particle size distribution of undeposited particle left inside the media shows that there is another
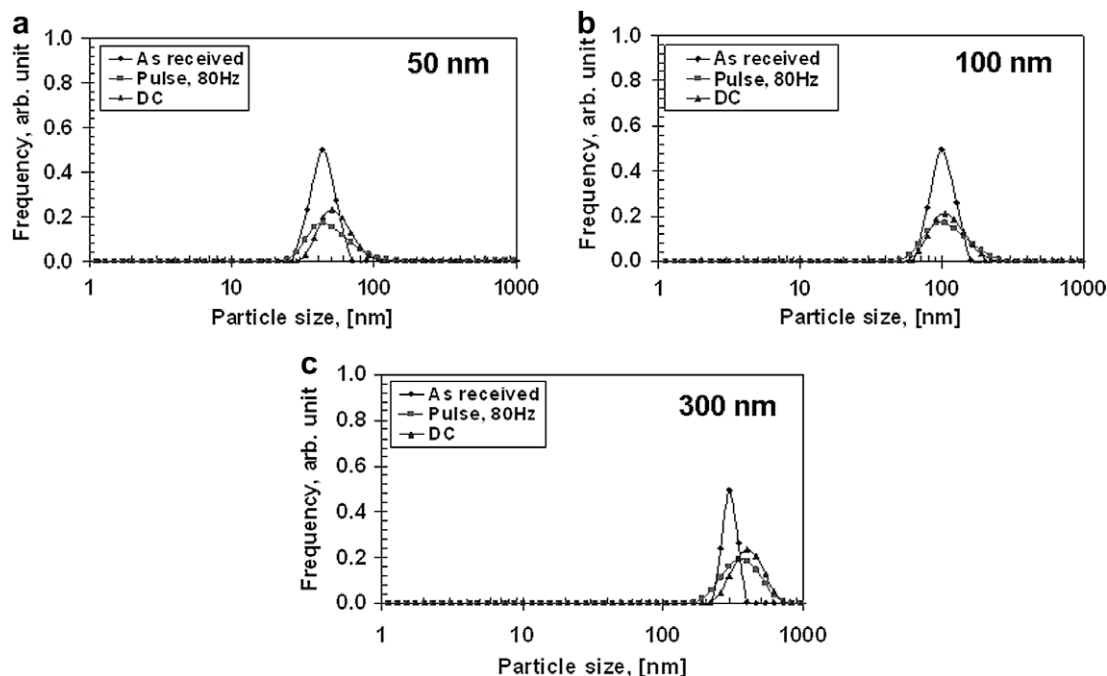
Fig. 7. Particle size distributions of PSL particles, (a) 50 nm, (b) 100 nm and (c) 300 nm. The initial particle size distribution (as received) is compared with the undeposited particles left in the media (pulse, 80 Hz and DC).

possibility of aggregation occurs in the suspension after DC charging in comparison with that of pulse DC charging (Fig. 7). This is ascribable to high particle–particle interaction or a change in the surface charge as they approach the electrodes. By using DLS, the as-received samples obtained in this study is compared with undeposited particles after 2 min of charging. A pulse DC charging with 80 Hz is chosen and compared with the conventional DC charging. The analysis shows that some aggregates are formed after the EPD is conducted. In most cases, the difference from its initial size distribution is larger in the case of conventional DC compared to pulse DC. During the charging, the electroosmosis eddy traps most of the attracted particles that gathered near the substrate vicinity as illustrated in Fig. 3. The trapped particles in the eddy are easy to collide with each other and aggregate. This phenomenon is similar to the "bridging", where the functional group at the polymer chains surface that is supposed to suspend the particles attached to nearby particles due to high compression force [20]. However, during the off-mode condition in pulse DC charging, the eddy is reduced or completely annihilated. Therefore, the particles that were treated by pulse DC charging seem to aggregate less significantly when the same parameter condition (i.e., applied voltage, deposition time) is conducted.

A comparison on the zeta potentials of as-received particles and undeposited particles left inside the media in Fig. 8 shows that the surface charge decreases after the EPD. The zeta potential values drop unevenly after comparison with its initial (as-received) value for all particles. The difference of zeta potential value is higher when small-size particles is conducted compare to large-size particle. As mention before, the large difference in zeta potential might due to high exposure time of different pH value that occurs at the very near of electrode vicinity. The pH value however, is difficult to measure because it depends on the chemical reaction rate of the ion dissociation such as water hydrolysis and other ionic species that available in the in the suspension. A large difference in the zeta potential value of the undeposited particles also might be the cause of particles aggregation as observed in Fig. 7. The large difference in zeta potential also shows that the particles are easy to be influenced by the charging condition and trapped in the eddy. With reference to Fig. 3, it is obvious that undeposited small-size particles can easily be trapped by the eddy created by the electroosmosis at the substrate vicinity, and hence changes its electrical properties. However, undeposited large-size particles such as 300 nm are hardly influenced by the electroosmotic eddy.
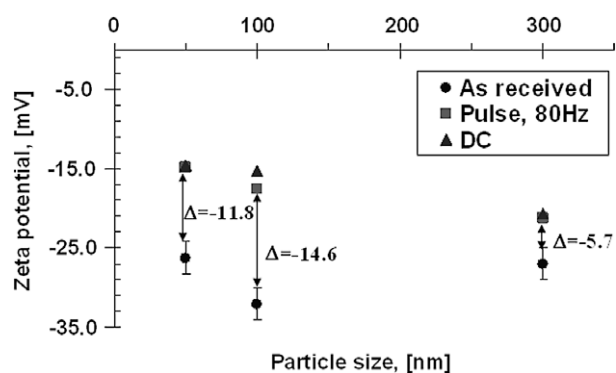
4. Conclusion

Disaggregation or aggregation of two-dimensional monolayer particles from aqueous suspended polystyrene latex (PSL) suspension can be controlled by implementing pulse DC charging EPD. High pulse frequency charging is found to be the key to reduce electrokinetic phenomena such as electroosmosis. Reduction of pulse charging frequency down to conventional DC charging can cause highly aggregated deposit particles.

Analysis of undeposited particles left in the media show the existence of electroosmosis eddy at the very near of electrode vicinity. The eddy caused the physical and electrical properties of

Fig. 8. Zeta potentials of three PSL particles, 50,100 and 300 nm before (as received) and after the deposition process (pulse, 80 Hz and DC). A conventional DC charging is also included for comparison.

nearby particles change from initial. Off-mode condition in pulse DC charging is found to be useful to reduce the existence of the electroosmosis eddy.

Acknowledgements

References

[1] P. Sarkar, P.S. Nicholson, J. Am. Ceram. Soc. 79 (1996).
[2] A.V. Delgado, F. Gonzalez-Caballero, R.J. Hunter, L.K. Koopal, J. Lyklema, J. Colloid Interface Sci. 309 (2007) 194–224.
[3] A.R. Boccaccini, F. Kaya, B. Su, B. Thomas, A.R. Boccaccini, Surf. Coat. Technol. 191 (2005) 303–310.
[4] S.P. Radko, M. Stastna, A. Chrambach, Electrophoresis 21 (2000) 3583–3592.
[5] V. Meille, Appl. Catal., A 315 (2006) 1–17.
[6] L. Besra, M. Liu, Prog. Mater. Sci. 52 (2007) 1–61.
[7] Y. Solomentsev, S.A. Guelcher, M. Bevan, J.L. Anderson, Langmuir 16 (2000) 9208–9216.
[8] M. Boehmer, Langmuir 12 (24) (1996) 5747–5750.
[9] Y. Solomentsev, M. Bohmer, J.L. Anderson, Langmuir 13 (1997) 6058–6068.
[10] H.J. Lee, S.Y. Yeo, S.H. Jeong, J. Mater. Sci. 38 (2003) 2199–2204.
[11] M.N. Naim, M. Kuwata, H. Kamiya, I.W. Lenggoro, J. Ceram. Soc. Jpn. 117 (2009) 127–132.
[12] P.M. Biesheuvel, H. Verweiji, J. Am. Ceram. Soc. 82 (6) (1999) 1451–1455.
[13] T. Pelberg, H. Versmold, J. Phys. Chem. 93 (1989) 5296–5301.
[14] H. Ohshima, J. Colloid Interface Sci. 248 (2002) 499–503.
[15] H. Ohshima, J. Colloid Interface Sci. 210 (1999) 397–399.
[16] S. Ghosal, Electrophoresis 25 (2004) 214–228.
[17] D.C. Prieve, Coll. Surf., A 250 (2004) 67–77.
[18] S. Raddice, P. Kern, H. Dietsch, S. Mischler, J. Michler, J. Colloid Interface Sci. 318 (2008) 264–270.
[19] W.L. Yu, F. Bouyer, M. Borkovec, J. Colloid Interface Sci. 241 (2001) 392–399.
[20] S. Asakura, F. Oosawa, J. Polym. Sci. 33 (1958) 183–192.