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Computer Simulation of Agglomeration by a Two-Dimensional Random Addition Model. IV.[1] Agglomeration Kinetics and Micromeritic Properties of Agglomerate of Binary Mixtures of Adhesive Circles

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Agglomeration of binary mixtures of adhesive circles with different sizes was simulated on a two-dimensional plane by a computer using a random addition model. The adhesion of circles in contact was determined by the probability coefficient of adhesion, P_c, defined by Eq. 1 in the text. It was assumed that the frequency of contact of circles was a function of the number of free circles that remained in the system. The growing process of the agglomerate was represented by the first-order kinetics Eq. 5 given in the text, describing a layering agglomeration. It was found that the agglomeration rate constant and the micromeritic properties of resultant agglomerates, *i.e.* porosity, average coordination number and shape, were determined by the probability coefficient of adhesion.

Keywords——agglomeration computer simulation; two-dimensional random addition model; agglomeration kinetics; layering agglomeration; coordination number; porosity; adhesion probability coefficient

Introduction

The present authors have been investigating the agglomeration mechanism of dispersed fine particles in liquid, so-called wet spherical agglomeration,[2-4] by computer simulation. The agglomeration models proposed by the authors for the simulations were random walk[5,6] and random addition[1,7] models. The former model was presented to simulate the changes in the agglomerate size, the size distribution and the agglomeration kinetics of poly-dispersed particles in a system. The latter one was useful to describe the changes in the shape and the internal structure of the agglomerate during agglomeration.

In the previous paper,[1] the authors simulated the closely packed agglomeration of heterogeneous binary circles on a two-dimensional plane using the random addition model. In that simulation, it was found that the growth rate of the agglomerate and the internal porosity of the agglomerate reached maximum at 50 to 60% of coarse circle fraction in the agglomerate. In the present study, the agglomeration of heterogeneous binary mixtures of adhesive circles was simulated to elucidate the relationship between the agglomeration kinetics, the micromeritic properties of the resultant agglomerate, such as shape, porosity and coordination number, and the adhesive property of circles.

Method

Agglomeration of Binary Mixtures of Adhesive Circles with Different Sizes——The method of simulation of the agglomeration was the same as described in the previous study.[1] At the start of the agglomeration, a fine circle was placed on the origin of a two-dimensional plane and another 249 free circles with arbitrary sizes were prepared in the system. Under centripetal force, the n-th ($n=2$, —249) circle among them successively approached the center circle from a random direction, which was determined by a pseudo random number, between 0 and 2π, generated by the computer. The type of approaching circle, *i.e.* coarse or fine, was determined by comparing the fraction of coarse circle ($0<C_r<1$) set in advance with a pseudo random number ($0<R_n\leqq 1$) generated by the computer. When $C_r\geqq R_n$, a coarse circle (diameter = 2, 3, 4 or 5) was assumed to approach, and otherwise a fine circle (diameter = 1) was assumed. The approaching circle followed a straight line passing through the origin until it encountered the first circle on the trajectory. Upon contact, it was decided whether the approaching circle adhered to the encountered one or not by comparing the probability coefficient of adhesion, P_c, with R_n generated by the computer. P_c was defined by Eq. 1 in the present study, since it was found that the size of agglomerate obtained from fine particles was larger than that from coarse particles in the previous experimental studies.[8,9]

$$P_c=(dD)^{-n} \quad (n=1.0,\ 1.2,\ 1.4,\ 1.6,\ 1.8,\ 2.0) \tag{1}$$

where D and d are the diameters of coarse and fine circles, respectively, and n is the moment. When $n=1$ or $n=2$, the agglomeration was controlled by the diameters or the surface areas of the newly contacted circles, respectively. As n increases, the agglomeration rate decreases and the resultant agglomerate is compacted more closely. When $P_c\geqq R_n$, the approaching circle adhered to the encountered circle; when $P_c<R_n$, the circle rolled around the circle already deposited, to approach the origin more closely, and reached the more stable (closest) position to the origin. Then, it was decided whether the circle adhered to the most stable position or not by using the same method as described above. When $P_c\geqq R_n$, the circle remained; when $P_c<R_n$ it was released from that position. At this point, unit agglomeration time was supposed to have elapsed. Thereafter a new $(n+1)$-th circle approached the origin and, followed the above procedure. The frequency of production of the new circle to be contacted was controlled by introducing the probability coefficient of generation of a circle, P_f, defined by Eq. 2.

$$P_f=N_f/N_{fo} \tag{2}$$

where N_f and N_{fo} ($=250$, in this study) are the numbers of free circles dispersed in the system at agglomeration times $t=t$ and $t=0$, respectively. When $P_f\geqq R_n$, a new circle approached; when $P_f<R_n$ no circle approached, but unit agglomeration time has elapsed. By this procedure, the frequency of the collision of particles decreased with the passage of agglomeration time. Therefore, in the present study the agglomeration rate depended on the probability of collision as well as on that of adhesion of the particles.

Determination of Diameter and Porosity of the Agglomerate——The diameter of the agglomerate was defined as the square root of the area of the agglomerate, S_a, which was defined as the area of a 360-gon inscribed in the periphery of the agglomerate. The porosity of the agglomerate (ε) was defined by Eq. 3.

$$\varepsilon=1-\frac{\pi(D^2N_{co}+d^2N_{fi})}{4S_a} \tag{3}$$

where D and d are the diameters of coarse and fine circles, respectively, and N_{fi} and N_{co} are the numbers of fine and coarse circles, respectively.

Results and Discussion

Growth Process of Agglomerate

Representative simulation results of the growth process of the agglomerate are illustrated in Fig. 1. At the initial stage, the agglomerate grew rapidly, and then the growth rate gradually decreased. It can be seen that the growth process of the agglomerate was determined by the moment, n, and the diameter of the circle in Eq. 1, which means that the probability coefficient of adhesion controlled the agglomeration behavior in Fig. 1. At the later stage ($t\geqq 10$), linear relationships between the logarithms of agglomerate size (D_a) and agglomeration time were found, as shown in Fig. 2. Therefore, the agglomeration kinetics were described by Eq. 4.

$$\log(D_a)=C_1\log(t)+C_2,\quad C_1=\log(D_{ai}/D_{aj})/\log(t_i/t_j) \text{ for } t\geqq 10 \tag{4}$$

Equation 4 is the kinetic equation derived by Kapur[10] for non-random coalescence

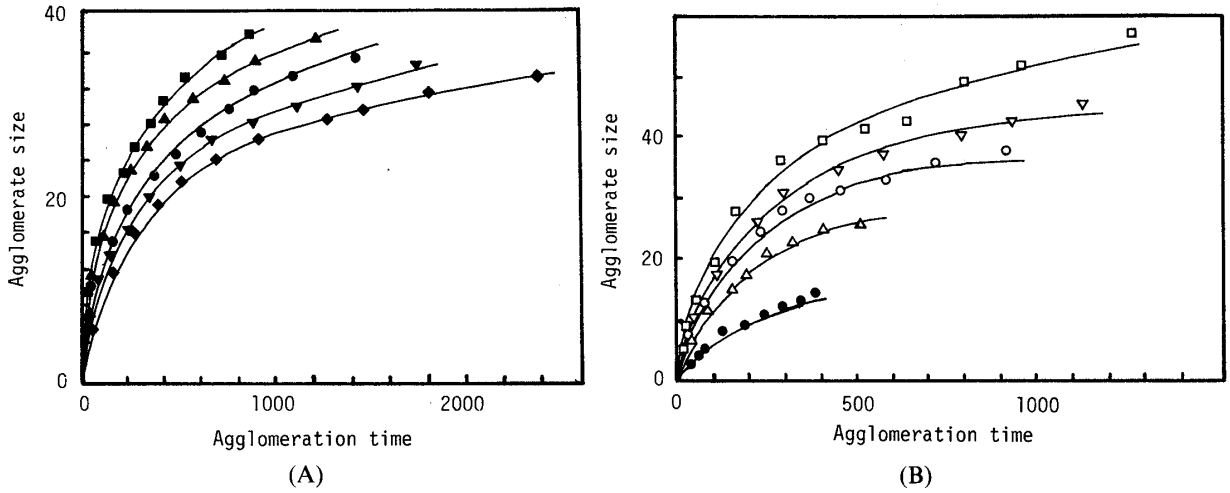

Fig. 1. Growth Process of the Agglomerate as a Function of Moment, n in Eq. 1 or Diameter of the Circles

(A) parameter; n, $C_r=0.82$, $Dd=3$, $n=$ ■ 1.0, ▲ 1.2, ● 1.4, ▼ 1.8, ◆ 2.0.
(B) parameter; Dd, $C_r=0.82$, $n=1$, $Dd=$ ● 1, △ 2, ○ 3, ▽ 4, □ 5.

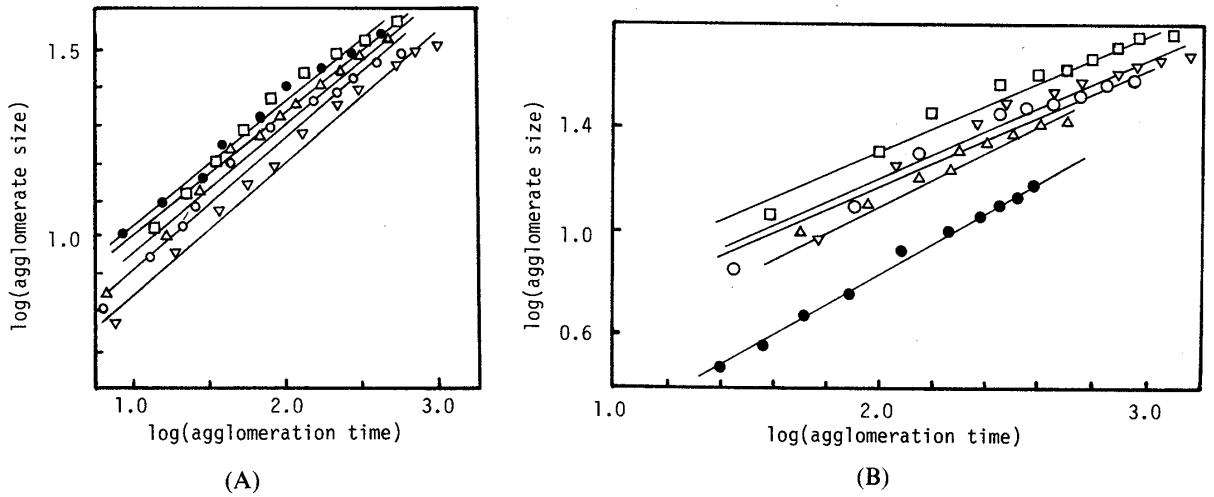

Fig. 2. Relationship between log(Agglomerate Size) and log(Agglomeration Time)

(A) parameter; n, $C_r=0.82$, $Dd=3$, $n=$ ● 1.0, □ 1.2, △ 1.4, ○ 1.8, ▽ 2.0.
(B) parameter; Dd, $C_r=0.82$, $n=1$, $Dd=$ ● 1, △ 2, ○ 3, ▽ 4, □ 5.

agglomeration. In Eq. 4, C_1 and C_2 are constants representing the dimensionless agglomeration rate and the log (agglomerate size) determined by extrapolating the straight line to $t=1$ in Fig. 2, respectively. C_2 relates to the coalescence rate at the beginning of agglomeration. Figures 1 and 2 suggested that the agglomeration mechanism at the initial stage was random coalescence which was strongly dependent on the probability coefficient of agglomeration, P_c, followed by layering agglomeration,[1] *i.e.* a non-random coalescence agglomeration. At the later stage, the preferential cohesion of a fine circle (=approaching circle) to the cumulative circle deposited on the origin (=coarse circle) was dominant, resulting in non-random coalescence agglomeration. The growth rate in the latter agglomeration was independent of P_c, since the slopes of straight lines in Fig. 2 were almost the same irrespective of P_c. It was also suggested that the particle diameter and the fraction of coarse particles were more important parameters to increase the initial growth rate of agglomeration than the surface area of particles in Fig. 1.

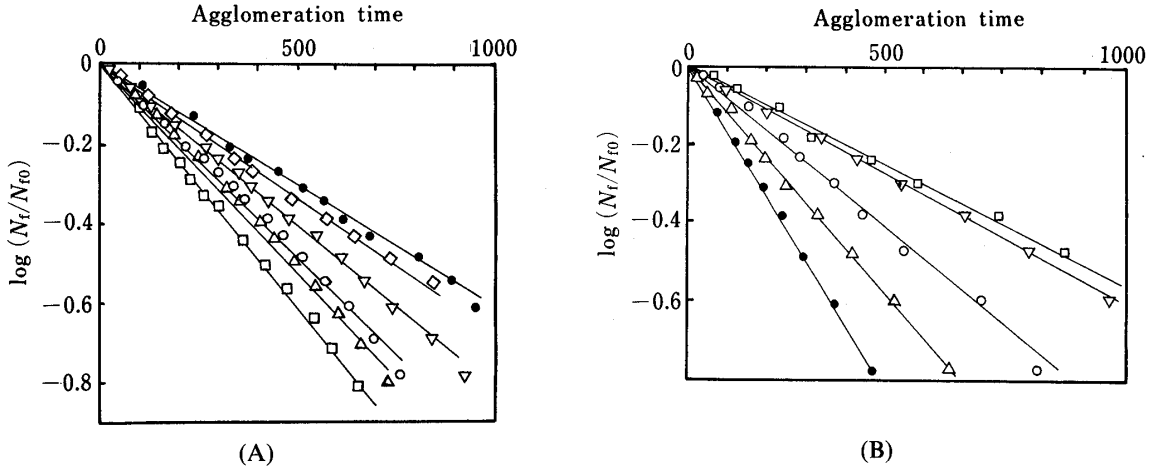

Fig. 3. First-Order Kinetic Plots of the Agglomeration Process

(A) parameter; n, C_r=0.82, Dd=2, n=□ 1.0, △ 1.2, ○ 1.4, ▽ 1.6, ◇ 1.8, ● 2.0.
(B) parameter; Dd, C_r=0.82, n=1, Dd=● 1, △ 2, ○ 3, ▽ 4, □ 5.

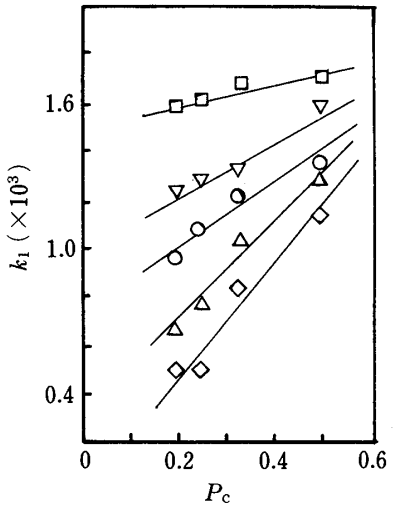

Fig. 4. Agglomeration Rate Constant as a Function of the Probability Coefficient of Adhesion

C_r=□ 0.09, ▽ 0.27, ○ 0.45, △ 0.64, ◇ 0.82.

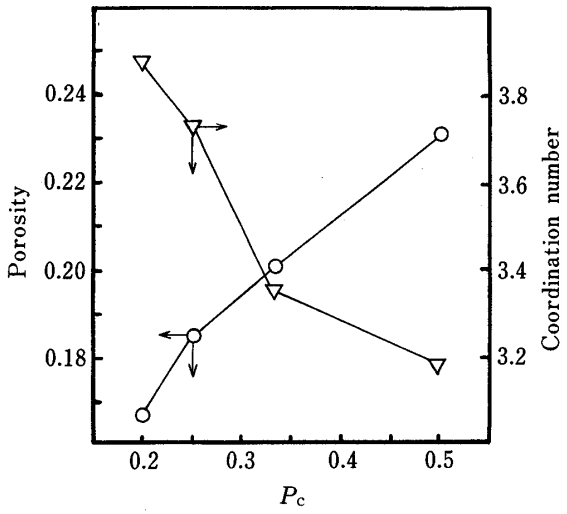

Fig. 5. Porosity and Average Coordination Number of the Agglomerate as a Function of the Probability Coefficient of Adhesion

Decrease of Particle Number in the System

Agglomeration kinetics can be represented in terms of the rate of decrease of the particle number in the system. A linear relationship between $\log(N_f/N_{fo})$ and agglomeration time (t) was found, as shown in Fig. 3. The findings in Fig. 3 indicated that the agglomeration kinetics at $t \geqq 10$ can be represented by the first-order kinetic Eq. 5, derived in the previous study[11] for describing layering agglomeration.

$$\log(N_f/N_{fo}) = -k_1 t \tag{5}$$

where k_1 is the agglomeration rate constant. This finding also supported the agglomeration mechanisms suggested in Figs. 1 and 2, *i.e.* random coalescence and non-random coalescence models at the initial and the later stages of agglomeration, respectively. In Fig. 3, it appears that the probability coefficient of adhesion of a particle, P_c, determined the agglomeration rate, which decreased with decreasing P_c. Particle diameter was an important parameter controlling the agglomeration kinetics as well as the moment, n, as can be seen in Fig. 3B. The

slopes of the straight lines in Fig. 3 are plotted against the probability coefficients of adhesion in Fig. 4. The agglomeration rate constant increased linearly with increase in the probability coefficient of adhesion. It was also found that the rate constant increased with decrease in the fraction of coarse particles in the system, C_r. The P_c-dependency of the agglomeration rate constant was enhanced with increasing C_r, as indicated by the steeper slopes of the lines in Fig. 4 at higher C_r.

Micromeritic Properties of the Agglomerate

It was found that the porosities and the average coordination numbers of the elementary circles in the agglomerates produced under various conditions were determined by the probability coefficient of adhesion defined by Eq. 1. Figure 5 shows the porosity and the average coordination number of the resultant agglomerate composed of 200 circles as a function of the probability coefficient of adhesion. In the present study, the porosity and the coordination number ranged from 0.16 to 0.24 and from 3.2 to 4.0, respectively. With increasing probability coefficient of adhesion, the porosity increased and the coordination number decreased linearly, which indicated that the coordination number increased linearly with the decrease in porosity, resulting in a more compacted agglomerate. It was also found that a more circular agglomerate was produced by decreasing the probability coefficient of adhesion.

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