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Computer Simulation of Agglomeration by a Two-dimensional Random Addition Model. II.[1] Agglomeration Kinetics and Micromeritic Properties of Agglomerates of Mono-sized Circles

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Computer simulation of agglomeration of mono-sized circles on a two-dimensional plane was undertaken by a random addition model to investigate the mechanism of agglomeration of dispersed particles in a liquid suspension. Under centripetal force, a new circle approached a circle placed on the origin from a random direction. Two types of agglomerations, *i.e.* closely and loosely packed agglomerations, were simulated by using different process of adhesion of the circles. For the closely packed agglomeration, the internal packing structure was independent of the probability coefficient of adhesion (P_r), but the agglomeration rate was P_r dependent. The packing structure and the agglomeration rate of loosely packed agglomeration were determined by the probability coefficient of adhesion (P_a). Heterogeneous agglomeration was also simulated by defining two types of circles, *e.g.* A and B, with different adhesion properties, which determined the internal composition and the structure of the agglomerate. By introducing the probability coefficient of collision (P_c), a practical agglomeration process in a batch system in which the residual numbers of particles decrease as the agglomeration proceeds could be described. A layering agglomeration could be visualized by defining P_c as n_f/n_{f0}. Population balance for this agglomeration led the rate equation expressed by equation (3) in the text. The agglomeration rates of loosely and closely packed agglomerations were determined in terms of P_a and P_r, respectively. The rate of heterogeneous agglomeration was less dependent upon P_a than the others. The internal packing structure of agglomerates strongly depended on P_a; when P_a increased, the porosity of the agglomerate increased and the average coordination number decreased. The porosity could be correlated qualitatively with the coordination number.

Keywords——computer simulation of agglomeration; two-dimensional random addition model; agglomeration kinetics; population balance; layering agglomeration; spherical agglomeration in liquid

Introduction

Computer simulation is an attractive method to analyze powder processing, since the boundary conditions and the participant parameters can be strictly controlled. Successful analyses have been made of powder processing procedures such as mixing,[2-4] packing,[5-7] sedimentation of particles,[8-9] *etc.* The present authors have been studying the mechanisms of agglomeration in liquid suspension, so-called wet spherical agglomeration[10-14] by Monte Carlo simulation on a digital computer.[15,16] The parameters determining the kinetics of particle growth were clarified by simulation of the random walk and random coalescence of circles on a two-dimensional plane.

In the present study, the simulation of agglomeration of mono-sized circles was undertaken to develop further the previous study[17] by a random addition model with reference to the method of Kausch *et al.*,[7] who simulated the random packing of noninteracting circles in a plane under the influence of a weak central force. In this paper, by causing interacting mono-sized circles to approach a core circle successively, various agglomerates were prepared from closely to loosely packed agglomerates. A new factor, *i.e.* collision factor, was also introduced

to control the kinetics of circle growth. The aim of the study was to clarify the effect of the adhesion factor on the micromeritic properties such as shape, internal structure and composition, and the growing process of agglomerates. Secondly, it was intended to visualize a layering agglomeration in a batch system by defining a suitable collision factor.

Methods

Closely Packed Agglomeration——For simulating the random addition of circles to a core in a plane, a weak centrifugal force was postulated to act on the circles. At the starting point, a circle was placed at the origin. The n-th($n=2,..99$) circle approached the center circle from a random direction, which was determined by a pseudo random number, between 0 and 2π, produced by the computer. The approaching circle followed a straight line passing through the origin until it encountered the first circle on the trajectory. Upon contact, the approaching circle rolled around the circle already deposited, to approach more closely to the origin. When the circle contacted another one during this rolling action, it was decided whether the circle would stop or roll further by examining whether the position contacted was stable or not, as illustrated in Fig. 1. If the position was unstable, the circle again rolled around the closer circle to the origin. This procedure was repeated until it reached a stable position. When the circle settled at the stable position, it was decided whether the circle remained there or not by comparing the probability coefficient of adhesion ($0<P_r\leqq 1$) with a pseudo random number ($0<R_n\leqq 1$) produced by the computer. When $R_n\leqq P_r$, the circle remained, otherwise it was released from that position. At this point, unit agglomeration time was supposed to have elapsed. By this means, the agglomeration time was counted. Thereafter a new $(n+1)$-th circle approached the origin and followed the above procedure. By repeating the procedure a desired number of times, an agglomerate composed of the desired number of circles could be prepared.

Loosely Packed Agglomeration——The general procedures for simulating loosely packed agglomeration followed the method for the closely packed one, except for the possible adhesion of circles at the first contact between the approaching circle and the deposited ones. When Rn was less than the probability coefficient of adhesion ($0<P_a\leqq 1$), the approaching n-th circle stuck to the first circle which was encountered on its path. After unit time had been added to the agglomeration time, $t\geqq 1$, a new $(n+1)$-th circle was allowed to approach the origin. When $R_n>P_a$, the approaching circle rolled around the deposited circle until it contacted another circle. At this point, it was decided again whether the circle adhered or not. When the circle adhered, unit agglomeration time was considered to have elapsed and the $(n+1)$-th circle yielded. Otherwise, it was examined whether that position was stable or not. When it was stable, the circle was released from the position and another new agglomeration was executed after counting unit time. When the position was unstable, the circle rolled further toward the center circle, and the above procedure was repeated. With increasing P_a, the agglomeration rate increased and a bulky agglomerate was produced.

Agglomeration of Heterogeneous Circles——When two kinds of circles, *e.g.* A and B, with uniform sizes but different adhesive properties approached the origin, an agglomerate with heterogeneous structure was produced. In this paper, the probability coefficients of adhesion between A and A, A and B, and B and B were set at Z ($0<Z<1$), 0.5 and 1-Z, respectively. The agglomeration procedure was the same as that for loosely packed agglomeration. The type of approaching circle was determined by comparing a random number produced by the computer with 0.5. When $R_n\leqq 0.5$ and $R_n>0.5$, the circle was defined as A and B, respectively.

Introduction of the Probability Coefficient of Collision——In a practical batch system of agglomeration, the particles are limited in numbers. Therefore as the agglomeration proceeds, the particle numbers in the system decrease. The frequency of collision of particles in the system depends upon the particle numbers, which determine the agglomeration rate. In this study, the frequency of collision of circles was regulated by reducing the frequency of production of approaching circles, which was conducted by introducing a new probability coefficient of collision, P_c. When $R_n\leqq P_c$, a new circle was produced to approach the center circle. When $R_n>P_c$, no circle was produced, but unit agglomeration time elapsed. In this study, P_c was defined in three different ways, *i.e.* $P_c=$ constant, $=n_f/n_{f0}$ or $=(n_f/n_{f0})^2$, where n_{f0} and n_f are the numbers of circles in the system at agglomeration times $t=0$ and $t=t$, respectively.

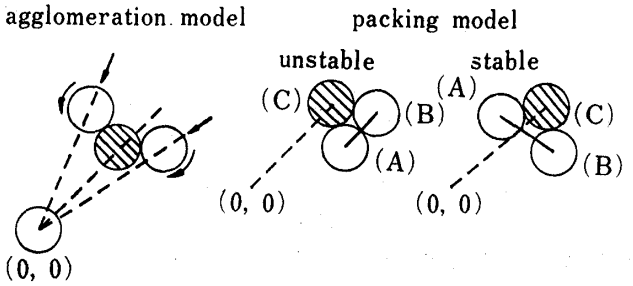

Fig. 1. Two-dimensional Random Addition Model for Simulation of Agglomeration

All simulations were repeated more than three times under the same conditions but using different initial conditions for producing pseudo random numbers. The variations of simulation results are illustrated by the standard deviation bars in the figures.

Results and Discussion

Analyses of Agglomeration Kinetics

The square roots of numbers of circles composing the agglomerate, which represents an equivalent diameter of the agglomerate, are plotted against agglomeration time as a function of the probability coefficient of collision in Fig. 2. In this case, the total number of circles in the system was set at 120. As expected, by introducing the probability coefficient of collision, the growth rate of the agglomerate decreased at the later stage in accordance with the decreasing probability of collision of circles. The reduction of the growth rate was enhanced by increasing the order of moment of n_f/n_{f0}. At the initial stage, however, the agglomeration followed the same process irrespective of whether the probability coefficient of collision was introduced or not. The introduction of the probability coefficient affected the agglomeration procedure in the same ways for both loosely and closely packed agglomerations.

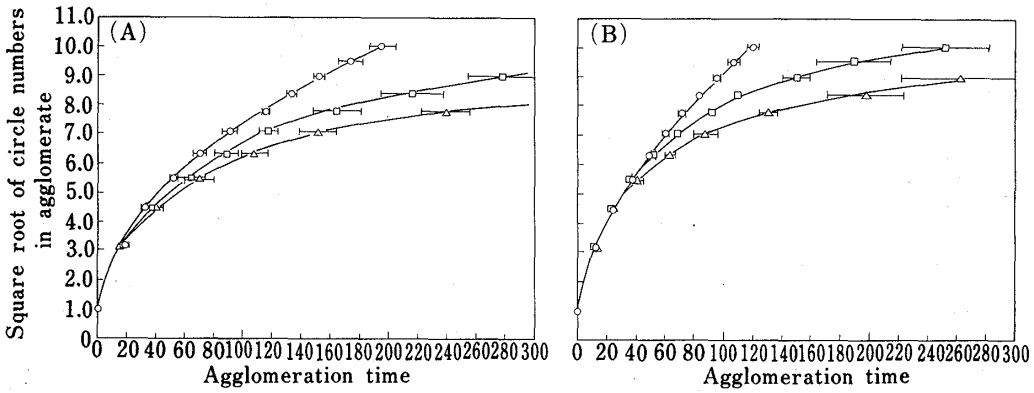

Fig. 2. Square Root of Circle Numbers in Agglomerate as a Function of Agglomeration Time

(A), Closely packed agglomeration, $P_r=0.5$
(B), Loosely packed agglomeration, $P_a=0.5$
Probability coefficient of collision: ○, 1.0; □, n_f/n_{f0}; △, $(n_f/n_{f0})^2$

The agglomeration behavior at the initial stage resembled random coalescence, since the diameter of the agglomerated circle was almost the same as that of the approaching circle. However, as the agglomerated circle grew, the difference in size of the two circles, *i.e.* agglomerated and approaching circles, became significant. Accordingly, the growth process of the agglomerate changed into a layering mechanism, in which fine circles adhere to large agglomerated circles. Therefore the population balance (12, 16) for agglomeration can be described by equation (1).

$$\frac{dN}{dt} = -k_1 n_f n_c - k_2 n_f^2 - k_3 n_c^2 \qquad (1)$$

Where N is the total numbers of circles in the system, n_f and n_c are the numbers of approaching and core circles, respectively, k_1, k_2, k_3 are the agglomeration rate constants and t is the agglomeration time. When the agglomeration process obeys a layering mechanism in which only fine circles corresponding to the approaching circle in this study preferentially adhere to coarse circles, *i.e.* agglomerated circles, equation (1) can be simplified to equation (2).

$$\frac{dN}{dt} = \frac{dn_f}{dt} = -k_1 n_f n_c = -K n_f \qquad (2)$$

Where $K=k_1 n_c$ is the agglomeration rate constant. The integrated form of equation (2) is equation (3).

$$\ln\left(\frac{n_f}{n_{f0}}\right) = -Kt \qquad (3)$$

Where n_{f0} is the initial number of circles in the system; at present $n_{f0}=120$.

The agglomeration kinetic plots of equation (3) for loosely and closely packed agglomerations are exhibited in Fig. 3. Irrespective of agglomeration type, only when the probability coefficient of collision was defined as n_f/n_{f0} did the kinetic plots become linear. This finding suggests that a layering agglomeration can be visualized by restricting the collision of circles by the factor, n_f/n_{f0}. In Fig. 4, the kinetic data of three types of agglomerations conducted under the condition of $P_c=n_f/n_{f0}$ are plotted as a function of the probability coefficient of adhesion, P_r or P_a. The slopes of the straight lines decreased with decreasing probability coefficients, which indicated that the agglomeration rate depended upon the probability coefficient. For the heterogeneous agglomeration, the agglomeration rate was less dependent upon the probability coefficient of adhesion than in the cases of the other two agglomerations.

The agglomeration rate constants represented by the slopes of straight lines in Fig. 4 were plotted against the probability coefficients of adhesion for three types of agglomerations. The agglomeration rate constants for closely packed agglomeration were linearly related to the probability coefficient of adhesion, P_r. When $P_r=1.0$, the agglomeration rate should coincide with that in the case of loosely packed agglomeration with the probability coefficient of adhesion, $P_a=1.0$, as shown in Figs. 5 (A) and (B). The agglomeration rate constants of loosely packed agglomeration exhibited a convex curve against the probability coefficient of adhesion. This finding was due to the fact that the probability of adhesion of circles for

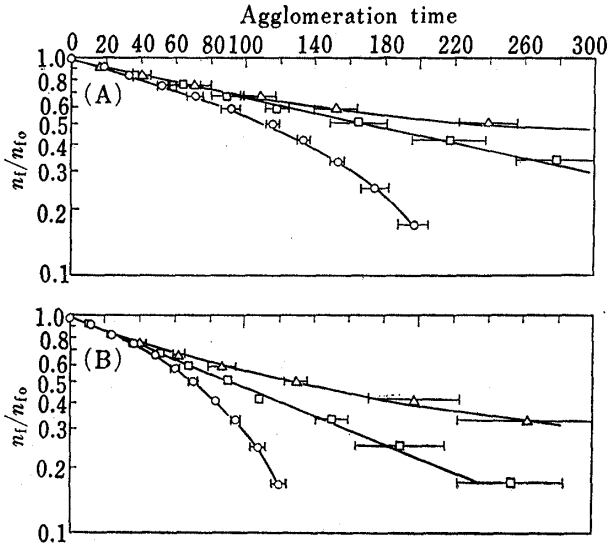

Fig. 3. Agglomeration Kinetic Plots as a Function of Probability Coefficient of Collision

(A), Closely packed agglomeration, $P_r=0.5$,
(B), Loosely packed agglomeration, $P_a=0.5$,
Probability coefficient of collision: ○, 1.0; □, n_f/n_{f0}; △, $(n_f/n_{f0})^2$.

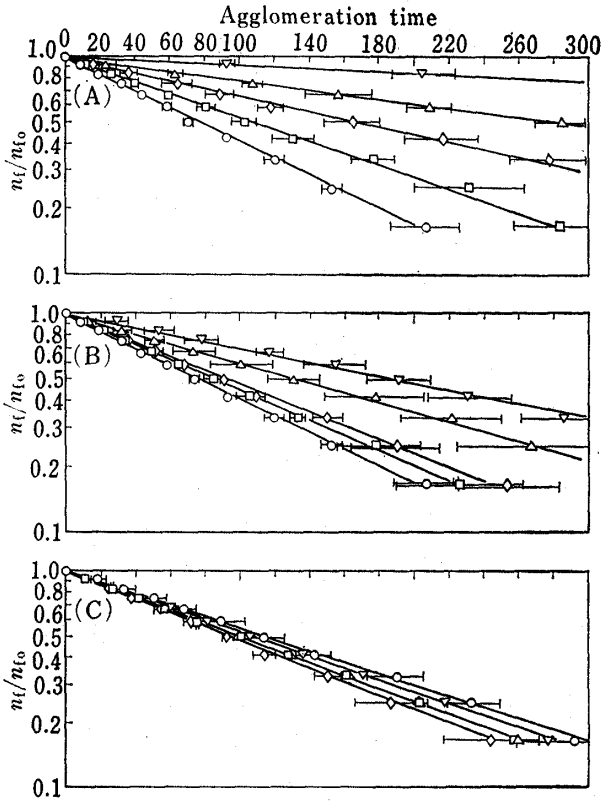

Fig. 4. Agglomeration Kinetic Plots as a Function of Probability Coefficient of Adhesion

(A), Closely packed agglomeration.
P_r: ○, 1.0; □, 0.7; ◇, 0.5; △, 0.3; ▽, 0.1.
(B), Loosely packed agglomeration.
Pa: ○, 1.0; □, 0.7; ◇, 0.5; △, 0.3; ▽· 0.2.
(C), Heterogeneous agglomeration.
Pa (A-A): ○, 0.9; □, 0.7; ◇, 0.5; △, 0.3; ▽, 0.1.

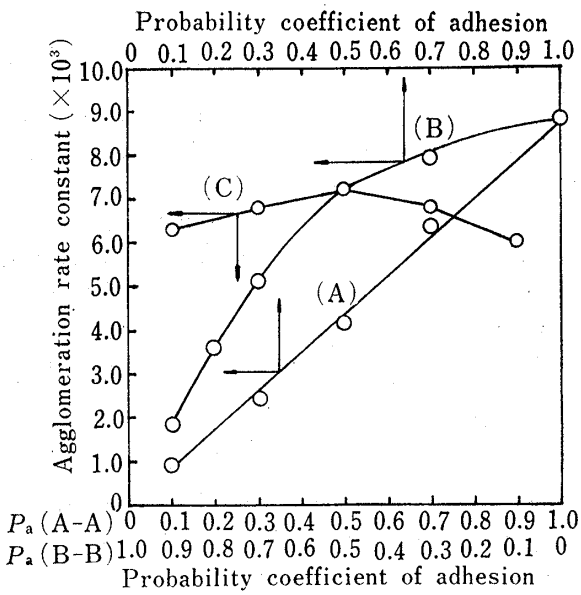

Fig. 5. Agglomeration Rate Constants as a Function of Probability Coefficient of Adhesion

(A), Closely packed agglomeration
(B), Loosely packed agglomeration
(C), Heterogeneous agglomeration

loosely packed agglomeration was higher than for the closely packed agglomeration when compared at the same values of P_a and P_r, as described earlier. The correlation curve of the agglomeration rate constants of the heterogenous agglomeration against the probability coefficient of adhesion in Fig. 5 (C) was symmetrical at P_a (A—A)=0.5, which corresponded to the loosely packed agglomeration of uniform circles at P_a=0.5 in Fig. 5 (B). Since the probability coefficient of adhesion of circles (P_a) was defined by equation (4), the symmetrical relation shown in Fig. 5 (C) resulted.

$$P_a = 1-Z \qquad (4)$$

Where Z is the probability coefficient of adhesion of the counter circle. Fig. 5 (C) indicates that the rate of heterogeneous agglomeration was higher at $P_a<0.5$, but was lower at $P_a>0.5$ than that of homogeneous agglomeration.

Micromeritic Properties of Resultant Agglomerates as Determined by Simulation

Representative simulation results for the three types of agglomeration restricted by $P_c=n_f/n_{f0}$ are shown in Fig. 6. Fig. 6 (A) represents a closely packed agglomerate composed of 100 unit circles, which was simulated with the probability coefficient of adhesion, P_r=0.5. The agglomerate was characterized by a compacted shape and a minimum interstitial void between component unit circles. The loosely packed agglomerate became bulkier with increasing propability coefficient of adhesion, as expected. The loosely packed agglomerates prepared with various values of the probability coefficient of adhesion, P_a=0.3, 0.7 and 0.9 are shown in Fig. 6 (B). One can see the large internal voids enclosed in the agglomerate compared with the closely packed agglomerate. The smaller values of coordination number as compared with the closely packed agglomerate were also a characteristic of loosely packed agglomerate. The heterogeneous agglomerate composed of circles A and B, prepared with the probability coefficient of adhesion, P_a=0.7 or 0.3, 0.5 and 0.3 or 0.7 for adhesion between A and A, A and B, and B and B, respectively, is displayed in Fig. 6 (C). It appears that the shape, the internal structure and the composition of agglomerates can be controlled by varying the probabilities of adhesion of circles.

To describe the effects of the probability of adhesion on the internal structure of agglomerates quantitatively, the correlation between the probability coefficient of adhesion and the porosity of agglomerates or the average coordination number of unit circles was investigated. The porosity of agglomerates was defined as the ratio of the interstitial void between the unit circles enclosed in the circumscribed circle of the agglomerate to its area. As the probability coefficient of adhesion increased from 0 to 1, correspondingly the porosity of the agglomerate (ε) increased, whereas the average coordination number of unit circles (n) decreased as shown in Fig. 7.

The relation between the porosity and the coordination number of the resultant agglomerate is shown in Fig. 8. The correlation curve obtained in this study was relatively lower than that of a real three-dimensional powder bed.[18] This deviation might be due to the

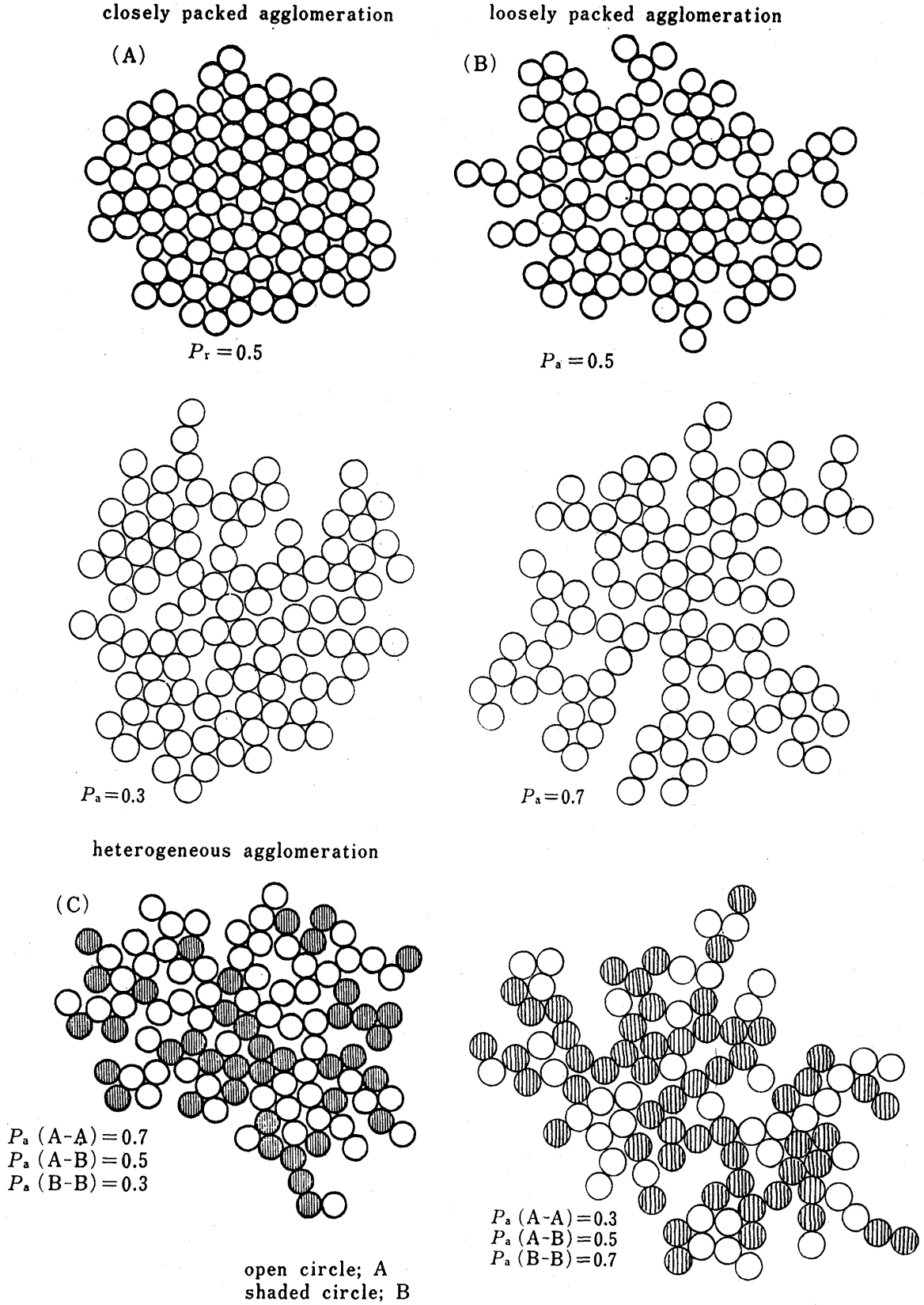

Fig. 6. Simulation Results

(A), Closely packed agglomeration, $P_r = 0.5$
(B), Loosely packed agglomeration, $P_a = 0.5$, 0.3 or 0.7
(C), Heterogeneous agglomeration, P_a(A-A) = 0.7 or 0.3
P_a(A-B) = 0.5; P_a(B-B) = 0.3 or 0.7 Open circle, A; shaded circle, B

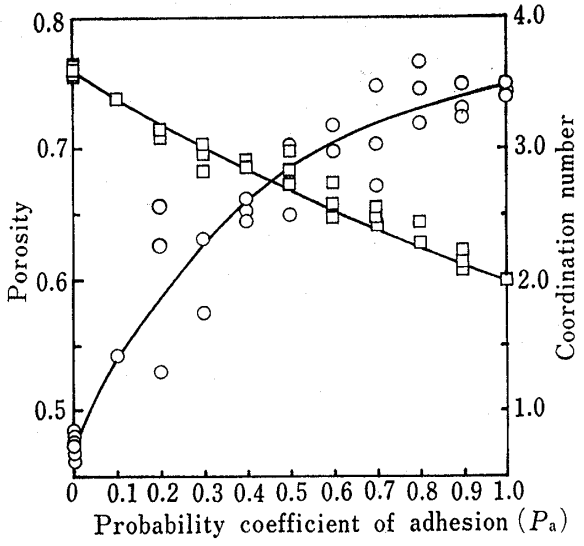

Fig. 7. Coordination Number and Porosity of Agglomerate as a Function of Probability Coefficient of Adhesion

○, porosity; □, coordination number
P_a=0 corresponds to closely packed agglomeration.

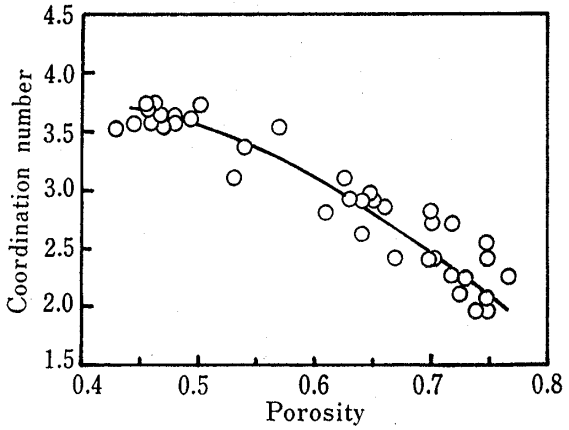

Fig. 8. Relationship between Coordination Number and Porosity of Agglomerate

difference in the mode of packing between them, since real three-dimensional particles can contact more adjacent particles than two-dimensional circles.

The agglomerations of two kinds of circles, A and B, with different adhesive properties and uniform size were conducted under the condition with the probability coefficient of adhesion, P_a=Z, 0.5 and 1-Z for adhesion between A and A, A and B, and B and B, respectively. The contents of A circles in the agglomerate varied in the range from 38 to 63%, depending upon the probability coefficient of adhesion between A and A, as shown in Fig. 9. The same trend was observed for circles B. The curves of the composition ratio of agglomerate against the probability coefficient of adhesion intercepted each other at the probability coefficient = 0.5, and were almost symmetrical with respect to this point. The average coordination numbers of unit circles in the heterogeneous agglomerate were almost the same for the all probability coefficients of adhesion, as can be seen in Fig. 10. The coordination number of

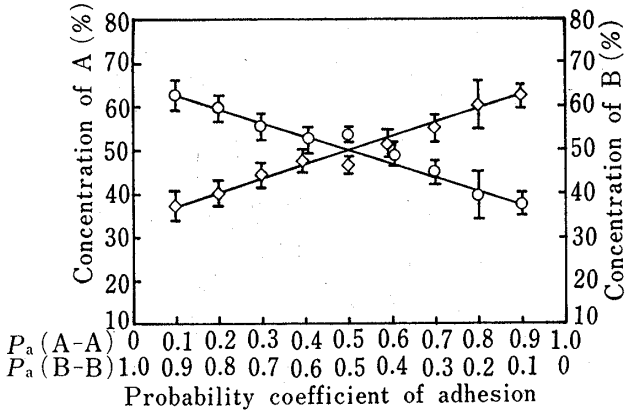

Fig. 9. Concentrations of A and B in Agglomerate as a Function of Probability Coefficient of Adhesion

Type of circle: ◇, A; ○, B.

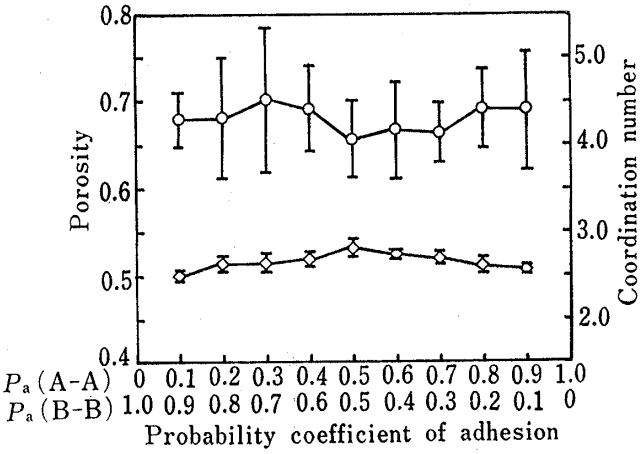

Fig. 10. Coordination Number and Porosity of Heterogeneous Agglomerate as a Function of Probability Coefficient of Adhesion

○, porosity; ◇, coordination number.

the heterogeneous agglomerate, *i.e.* 2.6 to 2.8, coincided with that of loosely packed agglomerate produced with the probability coefficient of adhesion=0.5. This indicates that the internal packing structure of heterogeneous agglomerate was independent of the probability coefficient of adhesion, whereas the composition of agglomerate was dependent upon it.

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