Coarse white polyethylene particles were coated by fine pigment particles of red iron oxide by high-speed rotational impact blending and by hand mixing in a mortar. As the dark pigments became progressively distributed over the coarse particle surfaces, the color characteristics of the resulting powder changed.

First, the effects of the mixing methods on the lightness, particle size and degree of mixing were investigated with respect to the treatment time and degree of mixing of the total mixture. The value of the degree of mixing was determined directly and precisely by chemical analysis. It was found that the degree of mixing increased with the treatment time at a certain mixing ratio of fine particles, corresponding to a coating ratio over coarse particles of less than 100% of closest packing on a number basis, but decreased at the mixing ratio of more than 100% by rotational impact. Micromixing to coat individual coarse particles was more easily and rapidly achieved by rotational impact blending as compared with hand mixing. Coating coarser particles at higher rotor speeds was more suitable for achieving homogenous mixing. In addition, it was found that the lightness of mixed particles decreased to lower than that by hand mixing due to the increased degree of mixing, but remained almost constant during the process of rotational impact blending, with its slight increase being due to embodiment of fine particles by frequent impact. This means that the lightness of particles reached a steady state in a very short mixing time, resulting in the reduction of the amount of fine particles for the same lightness effect when using the high-speed rotational impact blender.

Key-words: Coated particle, Mixing ratio, Degree of mixing, Lightness, Rotational impact blending

1. Introduction

The creation of new-generation materials by combining different powder materials has been of great importance, as indicated by the successful development of various composite materials and functional devices. Much of the research has been concentrated on the technology for covering core particle surfaces with fine particles mechanically by surface modification methods using grinding machines. Dry phase processing has several advantages as compared with the wet phase one. Therefore, a high-speed agitator-type mixer,¹ a high-speed rotational impact-type blender,² a ball mill³ and an attrition-type mill⁴ have been developed based on the mechanical principle of a dry system.

On the other hand, fundamental research has been extended by Alonso et al.,⁵–⁷ Shinohara and coworkers⁸–¹¹ and Naito and coworkers,¹²–¹⁴ and applications have been actively advanced in diverse fields.³¹ Since the basic research has just recently started, it is not easy to give a full description of the mechanism of the composite process.

The purpose of this work is to investigate the relationship between the mixing and lightness characteristics during the composite process of coarse and fine particles by high-speed rotational impact blending. In the past, Bannister and Harnby¹⁶ reported that the degree of extension of a fine colored ingredient could be followed by the measurement of the changes in the hue of the mixture. Recently, Satoh and coworkers¹⁷,¹⁸ and Endoh et al.¹⁹ proposed optical methods for characterizing a mixing process and the performance of powder mixers based on the measurement of changes in the lightness of the mixture, using a Theta-Composer devised by themselves. However, these attempts were mostly limited to low mixing ratios of fine to coarse particles. A quantitative analysis of the mixing degree, independent of the optical method which may be associated with the necessity of calibration or systematic errors, is still lacking.

Color properties are surface properties. In general, when a coarse particle is coated with fine particles, the surface properties of the resulting particles are different from the original ones and shift to the properties of the fine particles. They are influenced by the coating method and operational conditions as well as the mixing ratio.³⁰ In this study, we used a mixing ratio defined as the percentage of the area covered by fine particles on the surface of coarse particles, and found that the surface properties at mixing ratios greater than 100% exhibited different behaviors from those at ratios less than 100%. Furthermore, we calculated the degree of mixing independent of lightness, based precisely on a chemical analytical method, and then investigated how the lightness characteristics changes with the degree of mixing at the same total mixing ratio. For this purpose, a pigment of red iron oxide powder was used as the fine particles to coat the coarse polyethylene particles by high-speed rotational impact blending. In order to compare the effect of the mixing methods on the lightness, particle mixtures were also prepared by hand mixing in a mortar as an extreme case.
2. Experimental

2.1 Materials

Fine red Bengara powder (abbreviated as BG, Toda Co., principal ingredient Fe₂O₃, mean particle diameter 0.14 μm, lightness 35.4, true density 5.2 g/cm³) was used to coat coarse white particles of polyethylene (abbreviated as PE, Sumitomo Seika Co., mean particle diameters 40 and 180 μm, true density 0.918 g/cm³, lightness 90.6).

2.2 Apparatus

For the preparation of red BG-PE composite particles, Hybridizer¹ (NHS-0; Nara Machinery, Tokyo, Japan) was used, as schematically shown in Fig. 1. The machine is enclosed within a jacket through which heating medium or coolant is circulated. This hybridization process can be summarized as follows: the particles filled into the casing of Hybridizer are mixed and circulated in a high-speed air stream caused by the rotation of a rotor, and repeatedly collide with each other, the wall of the stator and the blades of the rotor. As a result of these mechanical actions, small particles are dispersed and fixed onto the surface of large particles. Hybridizer can be operated at various rotational speeds for a set period of treatment time.

2.3 Operations

(a) Hand mixing

For a given set of mixing ratios, mean diameters of PE particles and mixing time, PE and BG particles were weighed and transferred into a mortar. The mixture was stirred well by hand using a pestle for a given mixing time, and then the starting point of the mixing time was set to be 300 s for comparison. Total throughput was approximately 18 g.

(b) Mixing by rotational impact blender

For a given set of mixing ratios, mean diameters of particles and operational conditions, PE and BG particles were weighed and mixed in the mortar by hand for 5 min. The resulting premixture was then subjected to a mixing process by high-speed rotational impact blending with Hybridizer, lasting up to a given mixing time. The same total throughput as in hand mixing was used.

2.4 Measurements

(a) Mixing ratio

When the surface of a coarse particle is coated with a monolayer of fine particles, the number of fine particles, N, depends on their arrangement. The maximum value, Nₘ, corresponds to the case of hexagonal close packing on a plane and is given by

\[ N_m = \frac{2\pi}{\sqrt{3}} \left( \frac{D}{d} + 1 \right)^2 \]  

where D is the diameter of the coarse particle and d is the diameter of the fine particle.

In this paper, the total mixing ratio is defined as the percentage of the number of fine particles, N, versus Nₘ for each coarse particle.

(b) Degree of mixing

The following equation² was used to express the degree of mixing, M, corresponding to the coefficient of variation of the content of a key component. Thus, the larger the value of M, the more homogenous the mixture.

\[ M = -\log \left( 1 - \frac{1}{n} \sum_{i=1}^{n} \left( \frac{C_i}{C_o} \right)^2 \right)^{1/2} \]

n is the number of spot samples taken from a mixture containing a mean volume fraction of BG particles or feed, C_o and C_i is the BG content of any sample on a particle volume basis.

The volume fraction, C_i, was determined as follows. From one type of particle mixture, 120 mg was weighed and suspended in 2.5 ml 36% HCl and 30 ml water for one night to dissolve the red iron oxide. Then after the separation of PE particles from the solution by passing through a filter, the filtrate was analyzed by the phenanthroline colorimetric method to calculate the total amount of dissolved red iron oxide. A set of 10 samples from each type of mixture was measured to obtain C_i.

(c) Lightness of particle mixture

The lightness of a particle mixture was measured with a spectrophotometer (Shimadzu Corp., UV2400PC), calibrated by the manufacturer to the JIS (Japanese Industrial Standards) based upon the CIE 1976 standards (Commission Internationale de l'Eclairage). Every value of lightness reported in this paper is the average of 10 measurements at different points in a sample cell with a 7 mm beam diameter.

3. Results and discussion

3.1 Effect of mixing ratios on degree of mixing

The variation of the degree of mixing M with treatment time was influenced by the mixing ratio. In the case of rotational impact blending shown in Fig. 2, the value of M increased with mixing time at mixing ratios less than 100%, and then became constant after a certain time. However,
the trend of variation was different at mixing ratios greater than 100%. At the mixing ratio of 200%, the value of \( M \) first increased and then decreased with treatment time. At 430%, the value of \( M \) always decreased with increasing mixing time. On the other hand, at 100%, the value of \( M \) fluctuated slightly around 2.9.

These results indicate that interacting forces between coarse and fine particles due to, capillary, van der Waals or electrostatic forces, are different during the mixing process at mixing ratios less and larger than 100%. In the case of ordinary mixing where there are large differences in particle size and the mixing ratio, fine and coarse particles tend to segregate. When the interacting force between particles is negligible, segregation will become predominant. However, in the case of rotational impact blending, at mixing ratios less than 100%, theoretically, every fine particle can adhere onto the surface of a coarse particle in a monolayer up to the closest packing arrangement, and the interacting force between the large and fine particles is the main driving force for coating or mixing throughout the entire process. Therefore, the longer the mixing time, the more homogenous the mixing by the transfer of free particles onto the coarse particle surface. Then the degree of mixing, as well as the coating ratio, saturated after a certain time at which the coating of particles was completed.

Meanwhile, at mixing ratios larger than 100%, free fine particles still remained after complete coating. The interacting force between the free particles and the completely coated coarse particles should be much less significant comparing with the above case. Consequently, segregation became predominant, and the degree of mixing decreased with mixing time.

On the other hand, the fluctuation of \( M \) at 100% can be explained as follows. The mixing ratio of 100% is the critical point of complete coating, as defined in Section 2.4, and the coarse particles PE are comprised of a Gaussian distribution of particle sizes. When mixing ratios much less or larger than 100%, the error caused by size distribution was ignored. However, at 100% the effect due to size distribution, that is, size segregation, would become significant, and thus the value of \( M \) would fluctuate.

It is also observed in Fig. 2 that the value of \( M \) decreased with increasing mixing ratio. At a higher mixing ratio, less free surface area of coarse particles exists for fine particles to redistribute, resulting in the reduction of the transfer rate of fine particles among the coarse ones. Hence, as the processing time becomes longer, the transfer probability of fine particles decreases because of their fixation effects on the coarse particle surface due to frequent impact. Consequently, the mixing degree cannot attain the maximum value corresponding to the mixing ratio.

Furthermore, the degree of mixing by rotational impact blending was higher compared with that by hand mixing at the same mixing ratio, as shown in Fig. 2. This is because stronger forces generated inside Hybridizer enable the dispersion of the smaller aggregates of fine particles that still remain after hand mixing. In other words, the micromixing that leads to the coating of individual coarse particles is more easily and rapidly achieved by means of Hybridizer due to a higher level of mechanical energy.

Figure 3 shows the SEM images of surface areas of PE particles (180 μm) covered with red iron oxide particles (0.14 μm) at different processing times for hand mixing and rotational impact blending. Comparing Figs. 3(a)–(d), it can be seen that the larger aggregates of fine particles were broken down into smaller ones by hand mixing and then dispersed to single particles until the embedment of fine particles by rotational impact blending. Consequently, there are two kinds of mixing mechanisms, micromixing on
the scale of individual coarse particles and macromixing with local segregation; thus a uniform and stable mixture of particles with a large size difference can be produced at mixing ratios less than 100% by rotational impact blending.

3.2 Effect of PE particle diameter and rotational speed on degree of mixing

Figure 4 indicates that the value of $M$ was lower for the smaller diameter of PE (40 μm), compared with that for the larger one of 180 μm at a mixing ratio of 10%. For coarser particles, the coating rate is higher, and the fine particles can be transferred to other coarse particles more easily. As a result, the mixture with larger PE more easily attained homogeneity.

Figure 5 shows the effect of the rotational speed of Hybridizer on the degree of mixing. It is found that the progress of mixing was faster at the higher rotational speed of 15800 rpm. It can be considered that the impact, shearing, and frictional forces among particles were stronger and the mobility of fine particles was higher in comparison with the case at 13200 rpm.

3.3 Relationship between lightness and degree of mixing

Figure 6 shows the plots of lightness against the degree of mixing at different mixing ratios of the particle mixture. It is noted that the particles prepared by means of Hybridizer were much darker compared with those prepared by hand mixing at the same mixing ratio. This means that the complex set of forces generated inside Hybridizer enables the smaller aggregates of fine particles that still remain after hand mixing to disperse to a greater extent, which results in an increase in the dark coated area (see also Figs. 3(a)–(c)). Therefore, as the mixing became more homogeneous, the lightness decreased. It also illustrates a feature of rotational impact blending that the lightness slightly increased with the degree of mixing due to embedment, as shown in SEM micrographs in Figs. 3(c)–(d). Furthermore, it is also noted in Fig. 6 that the lightness at mixing ratios larger than 100% was lower than that of the original pure BG (35.4). Without mixing with PE, pure BG powders exhibit poor dispersibility and usually form aggregates. However, through the mixing process, these aggregates of fine particles are broken down on the surface of coarse particles by the mechanism mentioned above, and hence the nominal particle size of fine particles becomes smaller. According to Mie’s theory, smaller particles have a greater light scattering effect than larger particles. As a result, the lightness of mixing powders at mixing ratios larger than 100% could be lower than that of the original pure BG powders. The detailed discussion will be given elsewhere.

Satoh and coworkers investigated the relationship between the lightness of the processed powder and the mixing time for different mixers, such as the elliptical-rotor type, high-speed stirring type and high-speed shearing type, and found that the lightness decreased along a gentle curve as the processing time increased. Polymethyl methacrylate (50 μm) was used as core particles, and magnetite black (0.17 μm) as fine particles. In these cases, the lightness was an effective index for measuring the mixing characteristics with processing time.

However, in the case of Hybridizer, the behavior was different as shown in Fig. 6. During rotational impact blending, the lightness remained almost constant. This means that the lightness reaches a steady state in a very short time (about 5–20 s). Thus, the lightness would be an index for evaluating the mixing characteristics of different types of mixers, but it is difficult to characterize the mixing performance with time for the same mixer generating a high level of mechanical force, like Hybridizer. Consequently, it is necessary to relate the macroscopic powder characteristics such as lightness with the microscopic degree of mixing which is to be determined absolutely or...
independently of the lightness. Otherwise, the characteristics would include systematic errors of the optical device. Then, the macroscopic characteristics of the mixture would be enhanced further according to the higher degree of mixing in the microscopic sense, and controlled through the mixing ratio in a macroscopic sense.

From the standpoint of practical use, the results may be applied, for example, to create a new color, reduce fine pigment particle aggregation, and decrease processing costs by diluting an expensive pigment with coating to obtain the same effect.

4. Conclusions
In view of the results obtained in the course of the present work, the followings were revealed.

1) The variation of the degree of mixing with treatment time was influenced by the mixing ratio. The degree of mixing increased with time at mixing ratios less than 100% due to the transfer of fine particles to the coarse particle surface, but decreased due to the segregation effect at ratios larger than 100% with rotational impact blending.

2) Micromixing was more easily and rapidly achieved by means of Hybridizer due to a higher blending energy as compared with hand mixing. The use of Hybridizer to coat a coarse particle of larger mean diameter and to perform the coating run at a higher rotational speed was suitable to achieve homogeneity more quickly.

3) In the case of rotational impact blending, the lightness was much lower comparing with hand mixing at the same mixing ratio. However, in spite of the small increase in the degree of mixing, lightness remained almost constant, due to the embedment of fine particles by frequent impact during the process of rotational impact blending. This means that the lightness of particles reached its steady state within a very short period of treatment when using the high-speed rotational impact blender.

Acknowledgments The authors are grateful to Mr. S. Komatsu and Miss A. Ueno for their assistance in the experiments.

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