

## CHAPTER III

### THEORY

#### 3.1 Classification of mixing operations

In the manufacturing industries that handle powders, the operation of materials mixing is a necessary process for almost all of their manufacturing systems. This operation, however, is called by many names : mixing, mulling, kneading, agitation, milling, etc.

We will try to classify all kinds of mixing operations by principle into main categories and explain each category of operation. Mixing is generally divided as shown below :

- 1) Intermixing
- 2) Dispersing
- 3) Mixing-in

**Intermixing** is an operation which disperses different materials alternately in uniform array as shown in Fig. 3.1(a). It is not intended to change the initial particle shape or size in the material. This operation is the most popular and the simplest of the mixing operations. Usually it can be done sufficiently by a low-speed mixer. Intermixing is an operation to mix different materials homogeneously without changing their shapes. In the case of intermixing liquid materials, this operation is generally called " agitation".

**Dispersing** seems to be opposite of mixing, but this operation has become indispensable for fine mixing of modern powders composed of fine particles. Usually most of the fine powders are themselves agglomerates.

If mixing is performed simply by the simple intermixing operation, such powders will be mixed with no dispersion (disintegration) of agglomerates as shown in Fig. 3.1(b). It is for this reason that the action of dispersing these agglomerates is required in many cases. This dispersing operation, which seems to be unrelated to of mixing, is an indispensable condition for fine mixing.

The so-called "dispersive mixing," a combination of this dispersing action and the intermixing operation, enables fine mixing by breaking up the agglomerates into single particles and intermixing them homogeneously as shown in Fig. 3.1 (c).

**Mixing - in** is a process which requires intermixing and mixing-in at the same time. In this case, the afore-mentioned action of dispersing the agglomerates of powder particles is also required. Without this dispersing action, the surface coating action at the particle level as shown in Fig. 3.1 (d) may turn out imperfect, causing troubles to a subsequent process.

For this operation, high-speed shearing forces or pressing forces are required as is in the case of the dispersing process.

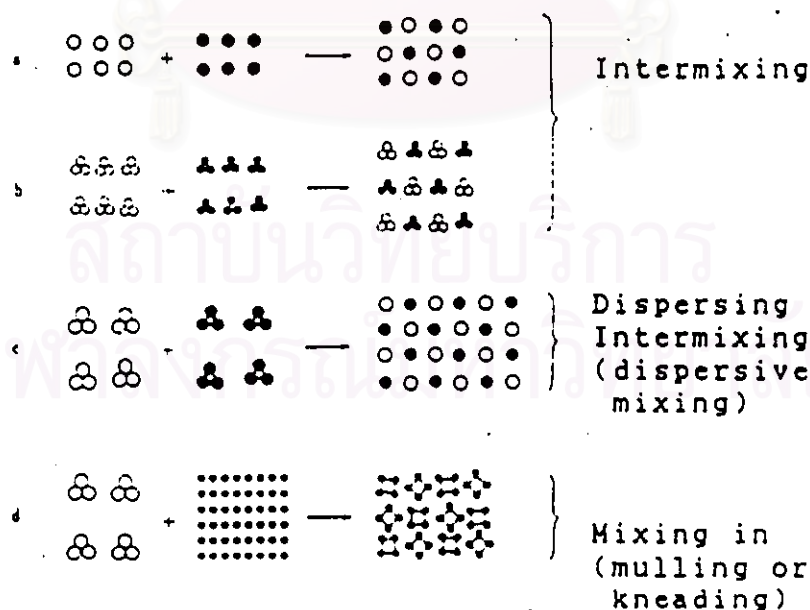


Figure 3.1 Classification of mixing operations

### 3.2 Dispersion (compounding) of additives in a matrix material

Dispersion is usually achieved through a combination of three mechanisms that all occur simultaneously (Ahmed, 1979) :

1. Initial wetting
2. Size reduction
3. Intimate wetting

**Initial wetting** is the formation of a mixture between a carrier and an additive. It is essential to every dispersion regardless of quality. At a minimum, it requires that the additive and carrier be sufficiently well mixed and have sufficient affinity for each other so that they would not separate when further work is applied to the system. The mutual affinity, compatibility, or wettability of two materials can be enhanced through a change in the surface characteristics of either or both, by the action of surfactants. Being of many different chemical types with different surface characteristics, additives would vary in the rate at which they wet out in a given system. Sometimes this is the controlling factor in the overall rate and the quality of dispersion that can be obtained regardless of the processing that follows. This varying nature of the additive also explains why no single surfactant is ideal for all dispersions. The importance of initial wetting is often underestimated because of the simple means by which it is usually obtained. Yet, initial wetting is not only essential, it often controls the quality of the final dispersion.

**Size reduction** is the process of breaking up the additive aggregates and agglomerates to primary particles. Studies of the processes which mix additives and plastics together have generally excluded the size-reduction mechanism from consideration, but the size reduction requires that sufficient mechanical energy be brought to bear on the particles to overcome forces holding them together. This energy is usually in the form of shear stresses developed in the matrix material,

which rupture the agglomerates. When these stresses (the magnitudes of which are determined by the viscosity of the matrix and the mixing conditions) are greater than some threshold value (which would depend upon the characteristics of the agglomerates and aggregates), size reduction will take place. If the stresses are smaller than that required to overcome the cohesive strength of the particles, the agglomerate would not break up. Because the consistency and tack of the matrix influence the effectiveness with which the mechanical energy could be transmitted to the particles, predispersion in a medium other than the base material is often considered.

The bonding energies between primary particles in aggregates and agglomerates vary considerably in strength. Variations in manufacture and treatment also produce different combinations of weak and strong fractions. For this reason, one additive might yield better results than another at low shearing stresses but be inferior at higher shearing stresses. Ratings at several levels of stresses for each dispersion attribute of importance are needed for a comprehensive evaluation of ease of dispersion.

**Intimate wetting** is the process of replacing air at the additive-air interface with a vehicle. This is of great importance in color-pigment applications requiring high transparency or maximum chroma in dark shades. Haze and reduced chroma are produced by light scattering at plastic/pigment interfaces if the wetting is incomplete. Effectiveness of shear transmission in the dispersion process also depends to a great degree on the amount of intimate wetting obtained. Shear provided by dispersion equipment through a fluid medium would have no effect on an aggregate unless a bond exists between the additive surface and the medium, and this is accomplished only through intimate wetting.

The same considerations discussed under initial wetting also apply to intimate wetting, i.e., a need for compatibility and the role of surfactants. However, intimate wetting is made more difficult by the much smaller particle sizes involved, particularly

for organic pigments with their high surface areas and microscopic interstitial pores. Such organic pigments often require extended dispersion cycles to achieve the desired results.

### **3.3 Ideal-case simulation of dispersion states in binary additive system**

Simulation is a powerful technique for solving a wide variety of problems. To simulate is to imitate the behavior of a system or phenomenon under study. The basic idea behind simulation is simple, namely, to model the given system by means of mathematical equations, and then determine its static and/or dynamic behavior. The simplicity of the approach, when combined with the computational power of a high speed digital computer, makes simulation a powerful tool. Normally, simulation is used when either an exact analytic expression for the behavior of the system under investigation is not available, or the analytic solution is too time-consuming or costly.

In modeling natural phenomena, two different approaches are available : deterministic and stochastic. Deterministic models are those in which each variable and parameter can be assigned a definite number, or a series of definite numbers, for any given set of conditions. In contrast, in stochastic or random models, uncertainty is introduced. The variables or parameters used to describe the structure of the elements (and the constraints) may not be precisely known. The former approach are less demanding computationally than the latter and could frequently be solved analytically.

P. In-eure (1994), W. Tanthapanichakoon (1995a), and N. Phingchin(1996) applied similar Monte-Carlo technique to simulate and evaluate the idealized dispersion states of a single-additive system using two kinds of fractal dimension. Experiments on the dispersion of iron oxide pigment in polyethylene resin and polystyrene resin [ P. In-eure 1994; N. Phingchin 1996 ] were also carried out and evaluated with the count-



based fractal dimension. In the present study, various dispersion states of a two-additive system were simulated using a combination of two ideal types of random patterns (uniform random and normal random dispersion), adhesion probability and location (angle) of adhesion.

### 3.3.1 Uniform random dispersion

In this ideal case of homogeneous mixture or uniform random dispersion, the uniformly random position  $(x, y)$  of a particle on a matrix material (a unit square) was simulated using the following mathematical formulas:

$$X = XRND * (X_{MAX} - X_{MIN}) \quad (3.1)$$

and

$$Y = YRND * (Y_{MAX} - Y_{MIN}) \quad (3.2)$$

where

$X$  = the position of the additive particle on the X axis

$Y$  = the position of the additive particle on the Y axis

$XRND, YRND$  = uniform random number between zero and

unity

### 3.3.2 Normal random dispersion

In the ideal case of Gaussian or normal random dispersion, the additive particles were randomly, though not uniformly, dispersed around the center  $(0.5, 0.5)$  of a matrix material. The mathematical formulas used to simulate the position  $(X, Y)$  of an additive particle in the matrix (a unit square) are as follows:

$$X = 0.5 + XRNG / 3.0 * (X_{MAX} - X_{MIN}) \quad (3.3)$$

and

$$Y = 0.5 + YRNG / 3.0 * (Y_{MAX} - Y_{MIN}) \quad (3.4)$$

where

XRNG, YRNG = standard normal random number  
(zero mean, unit variance)

X = the position of the additive particle on the X axis

Y = the position of the additive particle on the Y axis

The probability of XRNG or YRNG falling outside of (-3.0, 3.0) is quite small (< 0.26%)

Obviously, the statistical quality of the (pseudo-) random number generators used in the above simulations could significantly affect the results of computer experiments. Pijarn (1994) employed the typical uniform random number generator available on a personal computer (BASIC compiler). Since the detailed properties of the generator were unknown and no statistical tests have been carried out and reported on the properties, the present study decided to use the generators extensively tested by W. Tanthapanichakoon (1978).

### 3.3.3 Adhesion probability

In an ideal case of an ordered binary mixture, the value of the probability of adhesion is specified, which determines the probability that a new smaller additive particle is to adhere onto one of the larger core particles. A standard uniform random number is generated and compared with the adhesion probability value. If the former is less than the latter, the new smaller additive particle is designated to adhere onto one of the core particles, which is randomly chosen. The coordinates of the adhering particle is simulated as follows :

$$\theta = XRND * 2\pi \quad (3.5)$$

$$X' = RT * \cos\theta + X_A \quad (3.6)$$

and  $Y' = RT * \sin\theta + Y_A \quad (3.7)$

where

$\theta$  = the angle from the x-axis of the smaller adhering particle

$RT$  = radius of the adhering particle

$X_A$  = the position of the core particle on the X axis

$Y_A$  = the position of the core particle on the Y axis

$X'$  = the position on the X axis of the adhering particle on the core

particle

$Y'$  = the position on the Y axis of the adhering particle on the core

particle

On the other hand, if the new smaller additive particle is not designated to adhere onto any core particle, then the location of smaller additive particle in the unoccupied portion of the matrix is determined using either set of equations (3.1 and 3.2 or 3.3 and 3.4)

### 3.4 Indices of dispersion state

The following types of indices were applied in this work to the analysis of the simulated idealized dispersion states in order to illustrate the strength and weakness of each index type as applied to a binary ordered mixture.



### 3.4.1 Degree of mixedness

In compounding operations, a perfect homogeneous mixture is defined as one in which the additive component under investigation will statistically be uniformly dispersed throughout. Such a mixture is also called a perfectly random mixture. Statistical methods may be used to define the degree of mixedness (degree of homogeneity) of the compounded material. There are several definitions for this type of conventional statistical indices. In the present work, the following definition of the degree of mixedness is used as index to evaluate the dispersion state of an additive of interest :

$$M = 1 - \frac{\sigma_s}{\sigma_o} \quad (3.8)$$

Let  $x_i$  ( $i = 1, 2, \dots, N$ ) be the composition of the key component in the  $i$ -th sample of  $N$  spot samples taken randomly from a compounded material. The sample mean,  $\bar{x}_s$ , is given by

$$\bar{x}_s = \sum_{i=1}^N \frac{x_i}{N} \quad (3.9)$$

If the charged composition,  $\bar{x}_c$ , is known, the sampling procedure may be examined by comparing  $\bar{x}_s$  to  $\bar{x}_c$ . The sample variance,  $\sigma_s^2$ , is defined by

$$\sigma_s^2 = \sum_{i=1}^N \frac{(x_i - \bar{x}_s)^2}{N-1} \quad (3.10)$$

Obviously, the smaller the value of  $\sigma_s^2$  is, the closer to homogeneity the mixture is. Therefore, the degree of homogeneity in the mixture can be estimated by evaluating the value of sample variance  $\sigma_s^2$ . In other words,  $\sigma_s^2$  can be a useful measure of the degree of mixedness in practical applications. At the beginning of the compounding operation, where the additive and the matrix material are completely segregated, the value of  $\sigma_s^2$  is given by

$$\sigma_s^2 = \sigma_0^2 = \bar{x}_c(1 - \bar{x}_c) \quad (3.11)$$

The perfect homogeneous mixture in the compounding operation is defined as one with " the probability of finding the particle of the additive of interest being uniform everywhere in the compounded mixture". Such a mixture is called " a perfectly random mixture" and the value of  $\sigma_s^2$  as given by equation 3.10 is a minimum, ideally zero.

Here

- N = number of spot samples [-]
- $x_i$  = composition of the additive of interest in spot sample i [-]
- $\bar{x}_c$  = charged composition of the additive [-]
- $\bar{x}_s$  = sample mean of  $x_i$  [-]
- $\sigma_0^2$  = variance in the composition of the additive in a completely segregated system [-]
- $\sigma_s^2$  = sample variance (equation 3.10)

In some cases of manufacturing functional composite materials, more requirement than the state of ordinary homogeneous mixedness as shown in Fig. 3.2 is needed. The mixture is called an " ordered mixture " because " the composition of the bigger additive is uniform everywhere in the matrix and furthermore all of the smaller additive particles adhere onto each larger additive particle with the same probability ".



Fig. 3.2 Concept of the ordered mixture via random mixture

### 3.4.2 The fractal dimension

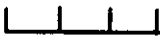
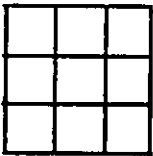
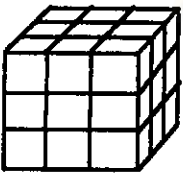
The fractal analysis method represents another type of quantitative methods to evaluate the extent of additive dispersion. "Fractal" comes from the Latin adjective "fractus", which has the same root as "fraction" and "fragment" and means "irregular or fragmented" (Mandelbrot, 1977). Mathematically a fractal is defined as a geometric shape that is made of parts similar to the whole in the same way, no matter how small it has been subdivided. This means that the shape of a fractal has self-similarity and a characteristic fractal dimension. The fractal dimension is a non-integer real number that represents the dimensionality of that fractal.

Even an object normally considered as one-dimensional, for example, a line straight segment, also possesses a self-similar scaling property. The line segment can be divided into  $N$  identical parts, each of which is scaled down by the ratio  $r = 1/N$  from the whole. Similarly, a two-dimensional object, such as a square area on a plane, can be divided in  $N$  self-similar parts, each of which is scaled down by a factor  $r = 1/N^{(1/2)}$ . A three-dimensional object, such as a solid cube, can be divided in  $N$  little cubes, each of which is scaled down by ratio  $r = 1/N^{(1/3)}$ .

With self-similarity the generalization of fractal dimension is straightforward. A  $D$ -dimensional self-similar object can always be divided into  $N$  smaller similar copies of itself, each of which was scaled down by a factor  $r$ , where  $r = 1/N^{(1/D)}$ . Conversely, given a self-similar object of  $N$  parts scaled by a ratio  $r$  from the whole, as given in Table 3.1, its fractal or similarity dimension is given by :

$$D = \frac{\log(N)}{\log(1/r)} = -\frac{\log(N)}{\log(r)} \quad (3.12)$$

Table 3.1 Scaling law for fractional dimension (Mandelbrot, 1977)

| Object  | Number of pieces (N) | Scaling (r)          | Law        |
|---|----------------------|----------------------|------------|
|    | 3                    | 1/3                  | $3 = 3^1$  |
|    | 9                    | $1/9^{(1/2)} = 1/3$  | $9 = 3^2$  |
|  | 27                   | $1/27^{(1/3)} = 1/3$ | $27 = 3^3$ |

In other words, the fractal is defined as an extremely irregular line (or surface) formed of an infinite number of similarly irregular sections (or parts). The fractal then has fractional dimension between one and two (or between two and three). It could be shown that an extremely complex shape might also be treated as a fractal, for example, the coastline (shoreline) of a country.

### 3.4.2.1 Count-based fractal dimension

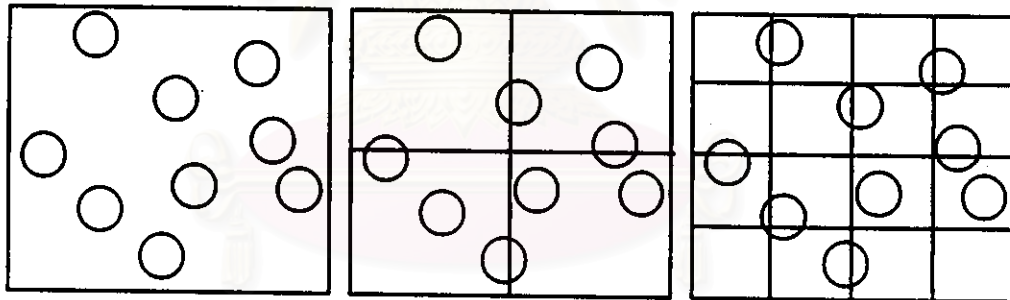
The square or rectangular cross section of a compounded material is divided into  $n \times n$  subsections ( $n$  : a positive integer). The number of subsections containing at least one particle of the additive of interest,  $N(n)$ , is counted as a function of  $n$ . Here  $n^{-1}$  is the similarity ratio.

If the system is a fractal, the following equation holds:

$$N(n) = (\text{Similarity ratio})^{-F_c} = (1/n)^{-F_c} \quad (3.13)$$

Thus the count-based fractal dimension,  $F_c$ , is defined by :

$$F_c = \frac{\log N(n)}{\log(n)} = -\frac{\log N(n)}{\log(1/n)} \quad (3.14)$$



|            |             |             |
|------------|-------------|-------------|
| $n = 1$    | $n = 2$     | $n = 4$     |
| $1/n = 1$  | $1/n = 1/2$ | $1/n = 1/4$ |
| $N(n) = 1$ | $N(n) = 4$  | $N(n) = 15$ |
| (a)        | (b)         | (c)         |

Figure 3.3 Determination of fractal dimension

In short, the count-based fractal dimension,  $F_c$ , is determined as the negative of the slope of the plot between  $\log N(n)$  and  $\log(1/n)$ .

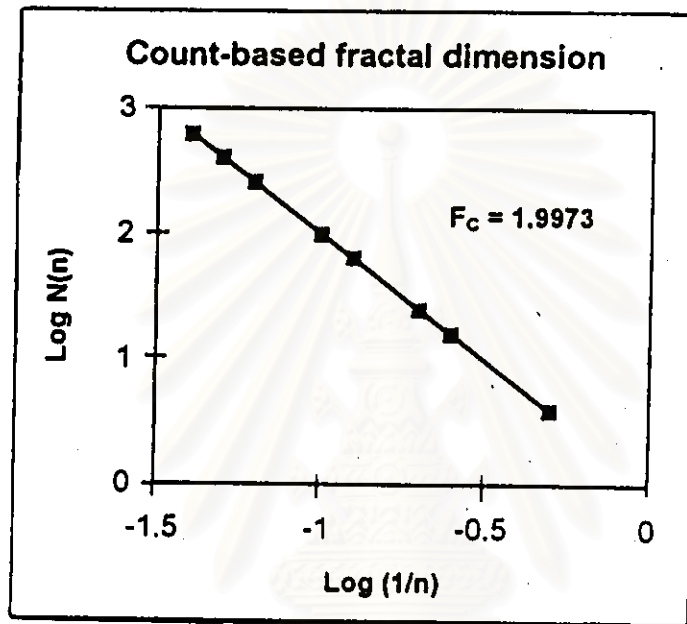


Figure 3.4 Example of count-based fractal dimension determination

#### 3.4.2.2 Area-based fractal dimension

Terashita, et al.(1993) are among the first researchers to apply the fractal analysis concept to evaluate the dispersion state of a compounded material. Their detailed observations of the large number of minute subsections to determine the fractal dimension were greatly aided with the use of an image analyzer system. A schematic diagram of the image analyzer system is shown in Figure 3.5.



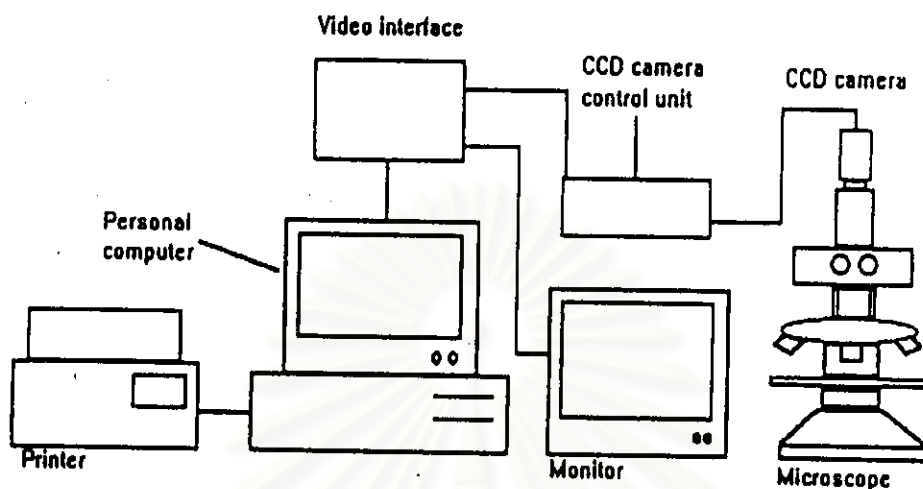


Figure 3.5 Schematic diagram of the image analyzer (Terashita, 1993)

Each sample of the compounded material was observed using light microscopy, and the obtained image was photographed using a CCD camera. The analog signal from the CCD camera was digitized and sent to a computer via a video interface. The obtained digital information was subjected to a smoothing treatment to remove noise before being converted to binary data to locate the particle-containing region on the dealt image. After these processings, the image was displayed on a CRT screen and used to calculate the fractal dimension. In this analysis, the magnifying power should be optimized to enable observation of the particle distribution over as wide a range as possible.

Following their approach, the area-based fractal dimension was adopted here as another quantitative representation of the dispersion state, as follows:

First, the simulated material was divided into  $n \times n$  equal rectangular segments ( $4 \leq n \leq 50$ ). Next, for segment no.  $i$ , the area ratio  $S_i(n)$  of additive particles was calculated as follows:

$$S_i(n) = \frac{A_i(n)}{A(n)} \quad (3.15)$$

$$\bar{S}(n) = \frac{1}{N} \sum_{i=1}^N S_i(n) \quad (3.16)$$

$$\sigma_s^2(n) = \sum_{i=1}^N \frac{(S_i(n) - \bar{S}(n))^2}{N-1} \quad (3.17)$$

where  $A_i(n)$  is the area occupied by the particles in segment no.  $i$ , and  $A(n)$  is the total area of the same segment.  $N$  is the number of sampled segments. A coefficient of variation  $D_s(n)$  was calculated from the mean value of  $S_i(n)$  for the applicable  $n$ , (namely  $\bar{S}(n)$ ) and the corresponding standard deviation  $\sigma_s(n)$  as follows.

$$D_s(n) = \frac{\sigma_s(n)}{\bar{S}(n)} \quad (3.18)$$

Next  $D_s(n)$  versus  $1/n$  was plotted on a log-log scale, and if  $D_s(n)$  and  $1/n$  bears the relationship :

$$D_s(n) \propto (1/n)^{-F_A} \quad (3.19)$$

then the particle dispersion state could be characterized by the area-based fractal dimension ( $F_A$ ).

When linearity was observed over the range of ( $4 \leq n \leq 50$ ), as shown in Figure 3.6, the area-based fractal dimension ( $F_A$ ) could be calculated from the slope. Naturally, the fractal dimension  $F_A$  increased as the particle dispersion state improved.

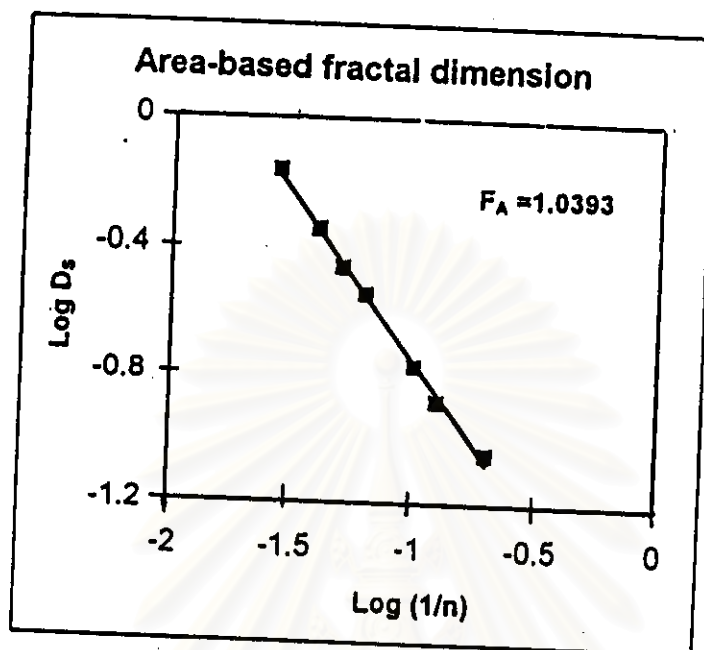


Figure 3.6 Example of calculation of the area-based fractal dimension

Figure 3.7 depicts two dealt images obtained by Terashita et. al. (1993) showing the filler dispersion state and its fractal dimension ( $D$ ). In this figure, black spots and smudged lines indicate fillers, while the white portions indicate the matrix resin. A high value of the fractal dimension demonstrated a visually good dispersion state with little filler aggregation. In other words, the fractal dimension proved useful in quantitative determination of additive dispersion state.

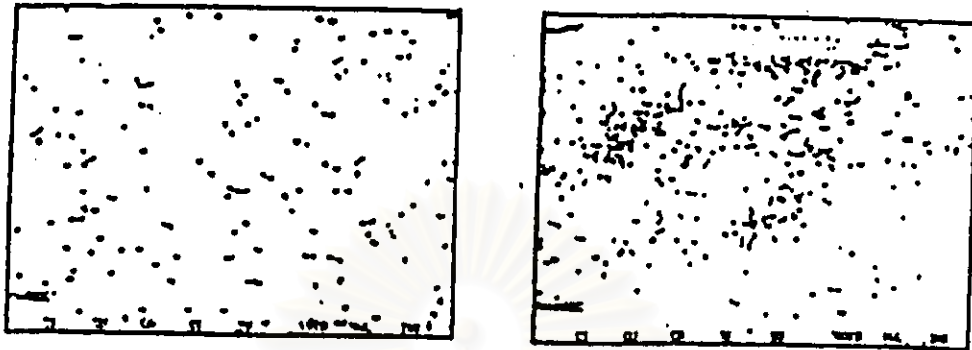
(a)  $D = 0.907$ (b)  $D = 0.462$ 

Figure 3.7 Dealt image showing filler dispersion state and its fractal dimension ( $D$ ) (Tarashita, 1993)

In the present work, the normalized fractal dimension is calculated by dividing the count-based fractal dimension and area-based fractal dimension with the corresponding value for uniform dispersion obtained by Phingchin (1996). In this way, the influence of the sample size (the number of observed additive particles in a sampled segment which corresponds to the charged concentration of the additive) can be eliminated.

### 3.4.3 Coordination Number

The coordination number is defined as the average number of small particles that adhere onto each core particle in the compounded material. For an ordered binary-additive mixture the coordination number should be a useful characteristic index.

In the present work, the mean value of the coordination number was calculated as the ratio of the total number of small particles adhering onto core particles divided by the total number of core particles. On the other hand, the mode value of the coordination number was obtained from the location of the peak of the frequency distribution of the number of small particles adhering onto each core particle.

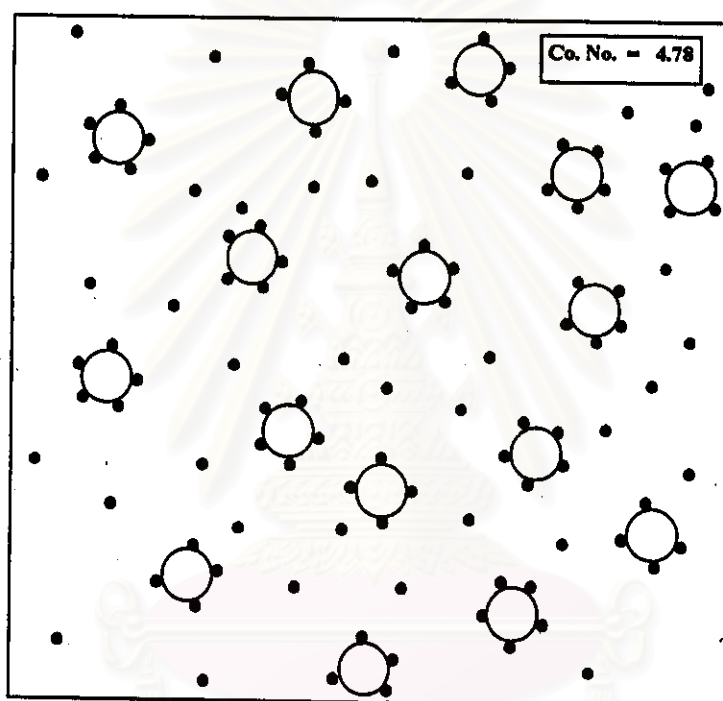


Figure 3.8 A simulated example of an ordered mixture  
(probability of adhesion = 50 %)

Figure 3.8 shows a simulated example of a partially ordered mixture. The ratio of small particles (black dots) to core particles (open circles) in the matrix was 10 : 1 while the probability of adhesion was 50 %. The observed coordination number (mean value) was 4.78.