CHAPTER II

LITERATURE REVIEW

The present work aims to develop and identify quantitative indices for evaluating the degree of dispersion of additives in compounded materials. Both novel and conventional concepts, such as fractal geometry, degree of mixedness and coordination number, are applied to the evaluation of various idealized dispersion states of additives in a matrix, which are simulated on a computer. Therefore, the present literature review will emphasize these related topics.

Lacey (1954) showed that all mixing machines for particulate materials utilize three principal mechanisms : (i) convective mixing, (ii) diffusive mixing and (iii) shear mixing. The concepts involved in analysing a perfect mixture (complete mixture) and partial mixtures (incomplete mixture) were examined and a statistically satisfactory expression evolved for the state of a mixture. A number of theories of the mixing rate were examined and compared with the few published experimental results, and a new theoretical treatment was offered based on a diffusion theory. It was shown to be in at least as good agreement with the facts as other existing theories, and to provide a better basis for extension to more complex cases.

Masumi Koishi (1979) studied a number of methods to modify a powder surface for the preparation of a highly functional powder. High functionality is important both to effective improvement and to new service applications of the original powder. A variety of technologies available for depositing, topochemically treating, mechanochemically treating, adsorbing and encapsulating coating and modifying surfaces were used as the methods to modify the powder surface. Depositing and adsorbing coating were used to improve the ease of dispersion of pigments in nonaqueous media, and to control their degree of flocculation. Topochemical and mechanochemical coating were capable of creating surface and near-surface properties distinct from the bulk properties. Mechanochemical encapsulation was used to modify, control and encapsulate the surfaces of various solids.

J. C. Graf (1991) applied the fractal dimension to characterize the structure of 224 lunar soil grains. The result shows that the fractal dimension can be used to successfully quantify the ruggedness of a particle, but fractal information is highly sensitive to resolution limits, and fractal interpretations without consideration of resolution can be misleading. To obtain a fractal dimension, a particle perimeter is measured many times with many different scales of measurement. The scale of measurement is called the stride length. With large stride lengths, the particle is modelled as a polygon with just a few sides of equal length; with small stride lengths, the particle is modelled as a polygon with several hundred sides of equal length. A decrease in the measurement stride length results in an increase in the estimated perimeter. The log-log plot of the stride length versus the perimeter estimate is called Richardson plot. The fractal dimension is $1.0+\beta$, where β is the value of the slope of the best-fit line of the plot. Sometimes one line can be drawn through all data points; its degree of ruggedness is the same for all the scales measured. Sometimes, particles have two fractal components with linear segments and two different slopes. The linear segment corresponding to large stride lengths is called the structure; the linear segment corresponding to small stride lengths is called the texture. The interpretation of fractal structures can be linked to the governing physical processes. A particle with different structural and textural fractal elements may have two different physical mechanisms forming two distinct values for ruggedness at different scales of observation.

The diagrams appear to be very different and the interpretations seem to be contradictory. These apparent contradictions are potentially misleading, but investigators can do things to minimize the confusion. There are four recommendations to remedy the problem of scale sensitivity: (I) Always scale all

Richardson diagrams using both absolute and Feret-normalized measures. (ii) Select a consistent upper bound as the maximum stride length. (iii) Use the highest possible resolution. (iv) Make interpretations with the help of physical models and physical processes.

Yoshihisa Mizuno, Keijiro Terashita and Kei Miyanami (1993) studied the operating plan for continuous kneading of an electrically conductive resin using analysis of time series. In continuous kneading, for stable-state production the feeder that feeds the raw material and the heater that heats the objective material must be controlled with consideration of the dynamics of the kneader. In their work, kneader dynamics was studied by examining the responses in the real time region and the frequency region, between variation of the feed rate (or kneading temperature) and variation of kneading torque, which represented the state of flow of the objective material. From this analysis, it was found that the response in the low-frequency region was most remarkable. The results showed that kneading could be performed in stable state by avoiding variation in the feed rate and heating. Continuous kneading of the electrically conductive resin was carried out with the control of the feeder that took the dynamics into consideration. It was confirmed that variation in the electrical conductivity of the electrically conductive resin could be made small, and that the effectiveness of control was remarkable when the flow state of the objective material in the kneader was plug flow.

Over the year the concept of fractal geometry has increasingly been applied to evaluate the degree of dispersion. The following summarizes its role and application.

Yoshihisa Mizuno, Keijiro Terashita and Kei Miyanami (1993) studied the evaluation of the dispersion state of an electrically conductive resin with fractal dimension. To determine quantitatively the dispersion state of the filler in the electrically conductive resin, the optical image of the dispersion state on a cross section of the resin was fed into a personal computer via an image processor and the fractal dimension of the dispersion state based on the area ratio was calculated. The fractal dimension was calculated for images of sixteen kinds and was effective in quantitative representation of the dispersion state. They also tried to evaluate the electrical conductivity of the electrically conductive resin with the fractal dimension. Electrical conductivity of the electrically conductive resin could be related to the product of the fractal dimension and the length of the filler. Prediction of the dispersion state was also attempted by comparing its fractal dimension, or the dimensionless number calculated from the data obtained during kneading.

Subsequently, Keijiro Terashita, Tetsuya Tanaka and Kei Miyanami (1993) studied the continuous kneading of electrically conductive composite materials and the evaluation of filler dispersion state. Using stainless steel fiber and metallized glass fiber as electrically conductive fillers, electrically conductive composite resins were prepared by continuous kneading.

Among the factors affecting the electro-conductivity of the composite material were the filler dispersion state and the filler length in the matrix resin. The key to excellent electroconductivity was to form an electrically conductive network ensuring long filler length, a uniform filler distribution and filler orientation in every direction. As quantitative indexes of the filler dispersion state, the fractal dimension and the direction ratio were used. A good filler dispersion state was obtained when the fractal dimension was high and the direction ratio was low. The electrically conductive composite resin was found to show excellent electroconductivity, irrespective of the filler type, provided that the filler length was long, the fractal dimension was high and the direction ratio was low. Uniform filler distribution and orientation with long filler length were obtained when the number of paddle revolutions N_t was low, the ratio τ/μ of shearing stress τ to resin viscosity μ was high and the ratio μ/V_h of μ to holdup V_h was low.

Another research which investigated the application of fractal geometry was presented by Yoshihisa Mizuno, Toshiyuki Shimizu, Keijiro Terashita and Kei Miyanami (1993). They evaluated the dispersion of filler in composite material. To design composite materials, and to optimize the manufacturing condition, quantitative evaluation of the dispersion state of the filler contained in composite materials was important. In their study, the batch kneading of thermosetting resin and circular particles and the continuous kneading of thermoplastic resins and electrically conductive fibers were performed, and the dispersion state in these composite materials was evaluated using the fractal dimension and the coordination number. According to the evaluation, the fillers were dispersed in a uniform state if the value of the fractal dimension was high, and aggregates of the fillers were broken substantially if the coordination number had a lower value. Based on the relation between the fractal dimension and the state of flow in the kneader as well as that between the coordination number and the state of flow, the kneading mechanism was discussed. It became clear that the aggregation of the fillers was broken preferentially if elastic mixing was performed, and the diffusion of the fillers in the material was accelerated if counter-flow or diffusional mixing was predominant. It was also pointed out that an excellent electrically conductive resin could be obtained when the product of the fractal dimension and the coordination number gave a high value.

Pijarn In-eure (1994) studies the effects of kneading conditions on the dispersion of pigments in polyethylene using a continuous kneader. The kneading temperature, the rolling temperature, the speed of rotation (twin screw), and the particle size of pigment particles were studied. This study used a convenient fractal analysis method to evaluate the dispersibility of pigment in polyethylene. In addition, evaluation methods to find a simple quantitative index of pigment dispersion have been studied. The experimental results showed that the higher the kneading temperature, the higher the dispersibility of pigment in polyethylene, but at the higher kneading temperature the process becomes more of mixing than dispersion. The dispersibility of the pigment increased as the rotational speed of the screw increased since a higher speed provided higher intensity of shear stresses to break down agglomerates of the pigment, so that the pigment could disperse better. Finally, the rolling temperature was found to have no significant effect on the dispersibility of the pigment. It only affected the internal structure between the pigment and polyethylene.

Ryuzo Itoh, Masanori Horizoe and Keishi Gotoh (1995) studied the application of the Voronoi polygonal analysis for evaluating the dispersed state of particles, where the coordinates of particle positions are measured and the Voronoi tessellation is conducted to obtain the distribution of cell areas. Although the method can provide precise data concerning particle dispersion, it has the demerit of being extremely time consuming. Hence this paper proposed a simple method to obtain the distribution of Voronoi cell areas from the measurement of the variation in local particle concentrations by a probe of adjustable size. Evaluation of the state of particle dispersion therefore became faster with the aid of TV monitoring systems.

Masanori Horizoe, Ryuzo Itoh and Keishi Gotoh (1995) studied the uniform dispersion of fine particles in a magnetic fluid and its evaluation. Particles confined in a thin horizontal layer of magnetic fluid were uniformly dispersed by applying a vertical magnetic field. The particle arrangements were observed both in experiments and in two-dispersional computer simulations. The regularity (R) of particle dispersion was defined as $R = \langle a \rangle^2/\sigma^2$ using the mean value $\langle a \rangle$ of the areas of the Voronoi polygons and its variance in the evaluation of the particle arrangements. The clusters of particles were virtually produced by uniformly swelling all of the particles. The distribution of the cluster size can be utilized for detailed evaluation of the particle arrangement. The regularity of the particle dispersion depends on the repulsive force acting between the particles. The uniformity of particle dispersion increases with the intensity of the magnetic field and the initial concentration of the particles.

Kenji Okada, Shin Akasaka, Hiroyuki Kurisaka and Yasuharu Akagi (1995) studied the rheological prediction of the dispersion of powder in ceramic injection molding mixtures. The process variables of mixing operation to improve the dispersion of powder in ceramic injection molding mixtures were examined for mixtures consisting of polyethylene and different kinds of ceramic powders. The dispersion in the mixtures mixed under various conditions was evaluated using the dynamic rheological measurement of the mixtures. The degree of dispersion in the mixtures was highly influenced by the mixing temperature and mixing speed of the mixer. With increasing mixing temperature the viscosity of the mixtures decreased, and the degree of dispersion in the mixtures was reduced as the agglomerate size became bigger. On the other hand, dispersion in the mixtures was improved with decreasing mixing temperature. This improvement in the dispersion resulted from the increase in the mixing strength of the mixer to break down agglomerates with increasing viscosity of the matrix. Increasing the mixing speed was also a processing parameters that improved the dispersion of powder in the mixtures. Furthermore, a simple rheological model was proposed to evaluate the mixing strength of the mixer to disperse the particles as a function of particle size and particle concentration.

Naorat Phingchin (1995) studied the effect of major factors on the dispersion of pigments in polystyrene upon using a continuous kneader and then determined the suitable the kneading conditions. The count-based fractal dimension was applied to evaluate the degree of dispersion of the pigment, which was either iron oxide or carbon black. In addition to the factors mentioned above, methods to simulate and evaluate the degree of pigment dispersion were studied for two ideal cases (uniform random and normal random mixing) with the use of the fractal dimension in the evaluation. The experimental results reveal that as the kneading temperature increased from 170 to

210 °C, the dispersion of pigment particles was enhanced. Furthermore, the higher the rotational speed of screw, the better the dispersion. This is because the higher rotational speed of the screw intensified shear stresses in the mixture, resulting in more breakage of the agglomerates and better dispersion. Moreover, the lower the feed rate, the higher the dispersion of pigment. The same trends were exhibited by both pigments. However, the observed values of the fractal dimension in the case of the carbon black were greater because the numbers of particles in the samples that were analyzed were greater, which corresponded the simulated ideal-case results (computer experiments). Even when the experimental values of the fractal dimension were normalized with the corresponding values obtained from the simulation, it was found that the normalized values of the fractal dimension in the case of carbon black were still greater. This may be attributed to the fact that carbon black which is organic has better compatibility with polystyrene than iron oxide which is inorganic.

Kazuo Ura, Hisakazu Shido (1996) proposed a mixing index based on the contact number obtained by coordination number sampling. The contact number is defined as the number of particles which are in contact with a particular particle called a specified particle. Statistically, the contact number mixing index is on the same basis as the first moment, which is in contrast to variance-based indexes. Also this work reported the distribution of the contact number for a binary mixture in an incompletely mixed state. The distribution was derived from a beta-binomial distribution as a conditional one. Furthermore, this paper extended the distribution of the contact number of a binary system to that for a multicomponent system. The precision of estimation of the mixing index was theoretically derived and compared with that of the reduced binary case. It could be concluded that the best precision was obtained if the particles whose population concentration was lowest were selected as specified particles. This conclusion held whatever the number of components in the system.

Arunya Thongchiew (1996) studied the factors influencing the dispersion of carbon black and quinacridone violet in high density polyethylene resin (HDPE) and determined the suitable kneading condition by applying the count-based fractal dimension to the evaluation of the dispersion state. In addition, effects of the kneading condition on the tensile properties of HDPE kneaded with either pigment were also investigated. The results show that the disperibility of either pigment increased as the kneading temperature and the rotational speed increased, and that the higher the feed rate was, the lower the dispersion state of the pigment became. The premix time, upwards of 10 minutes of preliminary mixing, had insignificant influence on the kneading result. As for the effect of the kneading temperature on the tensile properties of polyethylene with pigment, it was found that as the kneading temperature and the rotational speed of screw increased, the kneaded HDPE turned harder and more brittle, especially at kneading temperatures above 220 °C. Furthermore, comparison between the carbon black and quinacridone violet pigments revealed that the carbon black pigment, which had a smaller primary size (approximately one-sixth of that of quinacridone violet) and less polarity, exhibited more uniform dispersion state and better properties of the polymer blend.