# CHAPTER II

## LITERATURE REVIEW

The present work aims to study the effects of the dispersion state of pigments in a polymer on its utilization properties. The twin-screw kneader is used to compound pigments into a polymer matrix. A method for evaluating the dispersion state is based on the concept of fractal geometry. Therefore, this literature review will emphasize these related topics.

Daniel F. Mielcarek (1987) has reported about twin-screw compounding. Today's compounding equipment has made advanced plastics compounding a reality for polymer processors. The twin-screw extruder is a versatile tool, capable of handling a wide range of applications. In addition, its inherent shear, conveying, feeding and mixing characteristics have made it the machine of choice for the majority of today's sophisticated requirements. Without this flexibility, it might be necessary to sacrifice material quality to be able to compound at high levels. Other processing benefits are the ability to specify exactly where and how much shear input would be within the processing section and the ability to control the degree of mixing intensity by varying screw arrangements. With this versatility, it is possible to achieve optimum process conditions for even the most difficult mixing and compounding tasks, obtaining the desired end-product properties.

In 1988, Keijiro Terashita and Kei Miyanami (1988) studied about powder mixing and kneading. Relationship between powder properties and mixing state, which is important in the field of powder mixing, was investigated. It was clear that the mixing state (the degree of mixing) in a fixed-type mixer was hardly affected by particle size ratio and internal friction coefficient. In the case of tumbling mixer, suitable mixing conditions yielding a satisfactory mixing state of a mixture composed of different powder properties were suggested, and it was indicated that the mixing in this type of powder system was promoted by convective mixing and shearing mixing. As an example of kneading, kneading of magnetic recording materials was employed. The relationship between the kneading and the dispersion state as well as their evaluation methods were discussed. The state of kneading could be appreciated by observing of the coating state of the binder on the component particles and the state of dispersion could be evaluated using the square ratio and orientation ratio. A satisfactory kneading state contributed to good dispersion of magnetic powder materials and ensured high-grade videotape. In conclusion, it could be said that good quality of videotape depended on its kneading state.

Naruo Yabe, Keijiro Terashita, Kiichi Izumida and Kei Miyanami (1988) studied the dispersion of carbon black in resins by a continuous kneader and its assessment. A kneading experiment on thermoplastic resin and carbon black was carried out with a continuous kneader under various feeding rates. In addition to the measurements of the mixing torque in kneading and the residence time of the material, an assessment of the dispersion state of carbon black was attempted by means of image analysis and the validity of this method was examined. From the results, it was suggested that the degree of dispersion could be determined by the density of aggregation of kneaded material, and also it was clarified that the degree of dispersion in the kneaded material increased with a prolongation of the residence time, that is, the mixing action worked both radially and axially, or with an increase of the kneading energy.

C. J. B. Dobbin and W. E. Baker (1992) applied scanning electron microscopy (SEM) and image analysis techniques to analyze the dispersion quality in highly pigmented polymer systems. Their paper showed the use of scanning electron microscopy in conjunction with a commercial image analysis system to quantitatively characterize particle dispersion in polyethylene color concentrates. Compounds containing high loadings of organic and inorganic pigments were evaluated directly in order to avoid agglomerate reduction resulting from sample dilution. The effects of various processing conditions and additives on dispersion quality were also examined. The results showed that in the area of polymer color concentrates, the method and conditions of preparation had a fundamental effect on dispersion quality. In their study, two highly pigmented polyethylene systems had been examined using scanning electron microscopy with the resulting images characterized using computer-driven image analysis techniques. Agglomerate levels were determined numerically and correlated to process conditions. The effect of certain additives on pigment dispersion was also explored. Although clearly not applicable for routine quality control (QC), scanning electron microscopy coupled with image analysis provided a unique tool for examining the state of pigment dispersion in polymer concentrates.

In 1993, Takashi Teshima, Keijiro Terashita and Kei Miyanami (1993) studied the effect of pre-mixing time on the kneaded state of toner materials for their toning and charging characteristics. A pre-mixing experiment was carried out on toner materials with a high-speed type mixer using mixing time as variable. The obtained pre-mixture was kneaded under a specific condition, and then the kneaded material was pulverized and classified. On the basis of the evaluation of the kneaded state and charging characteristics, the effect of pre-mixing time was examined. The results show that the agglomerate area ratio in the kneaded material and the charge control agent (CCA) concentration on the surface of the toner particles enabled the assessment of the kneaded state and the consideration of the pre-mixing process. Furthermore, it was clarified that an excellent kneaded state was obtained at longer pre-mixing times, and the condition of CCA dispersion on the surface of the toner and the charging characteristics were determined by the kneaded state.

At approximately the same time, Takashi Teshima, Naruo Yabe, Keijiro Terashita and Kei Miyanami (1993) studied the mixing of toner composition and its evaluation. Thermoplastic resin, carbon black and a charge control agent (materials for toner) were mixed with a stir type mixer at various mixing times. The mixing process was investigated by measuring the load current of the motor and the temperature of the mixture during the mixing operation, and the state of the mixture were examined by SEM observation, X-ray microanalysis and so on. The results showed that the following processes, that is, the crushing of resin, the deagglomeration of carbon black and charge control agent, surface coating of the resin particles by the finer particles, and the reagglomeration of crushed resin simultaneously progressed during mixing. It was suggested that the state of the mixture obtained by pre-mixing contributed to the dispersion of carbon black and the charge control agent in the subsequent kneading process.

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 raw material and the heater that heats objective material must be controlled with consideration of the dynamics of the kneader. In their work, kneader dynamics was studied by examining 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 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 been was applied to evaluate the degree of dispersion. The following concern 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 image of the dispersion state on a cross section of the resin was fed into a personal computer from 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 fractal dimension and length of 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 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 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 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 $\tau/\mu$ of shearing stress $\tau$ to resin viscosity $\mu$ was high and the ratio $\mu/V_h$ of $\mu$ 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 the aggregation of the fillers was 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.

Recently, 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 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 stress to break agglomerates of the pigment, so that the pigment could disperse better than the smaller one. Finally, the rolling temperature had no significant effect on the dispersibility of the pigment. It only affected the internal structure between the pigment and polyethylene.

J. C. Graf (1991) applied the fractal dimension to characterize the structure of 224 lunar soil grains. The result shows that fractal 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. Decreases in the measurement stride length result in an increase in the estimated perimeter. The log-log plot of the stride length versus perimeter estimate is called Richardson plot. The fractal dimension is $1.0+\beta$, where $\beta$ 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 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 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.

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 time consuming. Hence this paper proposed a simple method to obtain the distribution of Voronoi cell areas from the measurement of variation in local particle concentrations by a probe of adjustable size. Evaluation of the state of particle dispersion therefore became faster for 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 of particle dispersion was defined by the mean value $\langle a \rangle$ of the areas of the Voronoi polygons and its variance, $R = \langle a \rangle^2/\sigma^2$, for 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 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 increased, and the degree of dispersion in the mixtures reduced as the particle size became smaller. On the other hands, 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.