Chapter III

Literature reviews

In this present study, the effects of the dispersibility of individual pigments in HDPE on its utilization properties using continuous twin-screw kneader are investigated. A method for evaluating the dispersion state is based on the concept of fractal geometry. Therefore, some studies related to this work are reported as follows.

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.

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 is known that the mixing state (the degree of mixing) in a fixed-type mixer is hardly affected by particle size ratio and internal friction coefficient. In case of tumbling mixer, suitable mixing conditions yielding a satisfactory dispersion 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 observation of the coating state of the binder on the component particles and the state of dispersion could be evaluated by 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 about dispersion of carbon black in resins by a continuous kneader and its assessment. A kneading experiment of thermoplastic resin with carbon black was carried out with a continuous kneader under various feeding rates. In addition to the measurements of the mixing torque required 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, as the mixing action worked both radially and axially, or with an increase of the kneading energy.

J. C. Graf (1991) applied the fractal dimension to characterize the structure of 224 lunar soil grains. The result showed that fractal could be used to successfully quantify the ruggedness of a particle, and that fractal information was highly sensitive to the resolution limits therefore fractal interpretations without consideration of the prevailing resolution could be misleading. To obtain the fractal dimension, a particle perimeter was measured many times with many different scales of measurement. The scale of the measurement is called the stride length. With large stride lengths, the particle was 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 stride length resulted 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 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.

C. J. B. Dobbin and W. E. Baker (1992) studied about analysis of dispersion quality in highly pigmented polymer systems using scanning electron microscopy and image analysis techniques. The paper showed the use of scanning electron microscopy (SEM) 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 were 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.

Yoshihisa Mizuno, Keijiro Terashita and Kei Miyanami (1993) studied the operating plan for continuous kneading of an electrically conductive resin with

analysis of time series. In continuous kneading, for stable-state production the feeder that feeds 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 responses in the real time region and the frequency region, between variation of 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 of feed rate and heating. Continuous kneading of the electrically conductive resin was carried out with control of the feeder that took the dynamics into consideration. It was confirmed that variation of 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.

Yoshihisa Mizuno, Keijiro Terashita and Kei Miyanami (1993) studied about evaluation of dispersion state of an electrically conductive resin using the fractal dimension. To determine the dispersion state of filler quantitatively 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 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 relate the electrical conductivity of the electrically conductive resin to the fractal dimension. Electrical conductivity of the electrically conductive resin could be related to the product of the fractal dimension and the length of filler. Prediction of the dispersion

state was also attempted by comparing the fractal dimension and the dimensionless number calculated from the data obtained during kneading.

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 the mixing time as variable. The obtained pre-mixture was kneaded under a definite 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 showed 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.

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 and 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 process, 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 states of the mixture obtained by pre-mixing contributed to the dispersion of carbon black and the charge control agent in subsequent kneading process.

Keijiro Terashita, Tetsuya Tanaka and Kei Miyanami (1993) studied about continuous kneading of electrically conductive composite materials and 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 electrically conductive 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 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 filler type, when the filler length was long, the fractal dimension was high and the direction ratio was low. A 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.

Yoshihisa Mizuno, Toshiyuki Shimizu, Keijiro Terashita and Kei Miyanami (1993) studied application of fractal dimension for evaluation of dispersion of filler in composite material. To design composite materials, and to optimize the manufacturing condition, quantitative evaluation of the dispersion state of 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 electric 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 electric conductive resin could be obtained when the product of the fractal dimension and the coordination number gave a high value.

Pijarn In-eure (1994) studied 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.

H. Ismail, P.K. Freakley, R.H. Bradley, I. Sutherland and E. Sheng (1995) studied the modes of action of a diamine salt of fatty acid referred to as a multifunctional additive (MFA) in carbon black filled natural rubber compound. The addition of MFA to a natural rubber compounded with 50 phr of N 330 carbon black was shown to increase certain physical properties up to a level of 2 phr (identified at the critical amount to coat the carbon black with a monolayer of MFA) after which there was a gradual deterioration of properties. The MFA exerted its greatest effect at the elastomer-carbon black interface as gum compounds showed minimal changes in mechanical properties with MFA concentration. In addition, this study indicated the importance of the dispersion of carbon black in matrix to the physical properties. Carbon black dispersion, measured by computer-aided image analysis and scanning electron microscopy (SEM) showed a substantial improvement with increasing MFA concentration. Bound rubber was found to decrease with the addition of MFA and a limiting bound rubber value was obtained at the MFA loading which corresponds to a monolayer coverage of the carbon black. This was attributed to a reduction of the amount of rubber immobilised in carbon black agglomerates due to the improved carbon black dispersion.

Kenji Okada , Shin Aksuka , Hiroyuki Kuriska and Yasuharu Akaji (1995) studied about the influence of mixing process variables on dispersion in injection molding mixtures consisting of polyethylene and different kinds of caramic powders and proposed a method of evaluating the dispersion state of the particles in the mixtures mixed at various mixing conditions using the dynamics rheological properties of the mixtures. The degree of dispersion in the mixtures was highly influenced by the mixing temperature and the mixing speed of a twin screw extruder. With increasing mixing temperatures , the viscosity of the mixtures increased due to the presence of agglomerates.

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 <a> 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 could be utilized for detailed evaluation of the particle arrangement. The regularity of the particle dispersion depended on the repulsive force acting between the particles. The uniformity of particle dispersion increased with the intensity of the magnetic field and the initial concentration of the particles.

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 were measured and the Voronoi tessellation was 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.

Naorat Phingchin (1996) investigated factors influencing the dispersion of pigments in polystyrene upon using a continuous twin-screw kneader to find the most suitable kneading conditions. This study also applied a fractal analysis method to evaluate the dispersibility of pigment. In addition, comparison between the experimental results and the corresponding ideal-case values obtained from the

computer simulation was studied. The experimental results showed that the higher the kneading temperature and the rotational speed of the screw, the higher the dispersion state of pigment in polystyrene, but as the feed rate of polystyrene-pigment mixture increased, the dispersibility decreased. Further more, the comparison result between the inorganic and organic pigment showed that the organic pigment (carbon black) dispersed more uniformly than the inorganic pigment (iron oxide) because the physicochemical properties of carbon black is more compatible with polystyrene than those of iron oxide.