CHAPTER III

THEORY

The subject of coloring polymers is an enormous field of study. The relevant points could be summarized as follows:

3.1 Polystyrene

Polystyrene has the simple repeating structure shown in Figure 3.1 and as might be expected from such a substantially linear polymer it is thermoplastic. As with polypropylene, PVC and other vinyl compounds there is the possibility of various stereoregular forms. Because of its amorphous nature the commercial polymer has for long been regarded as atactic. As with poly (methyl methacrylate) subsequent work has, however, indicated that the syndiotactic segments are more frequent than atactic segments and it appears that this may be a common feature of most free-radically initiated vinyl polymers. The specific position of the benzene ring is, however, sufficiently random to inhibit crystallisation.
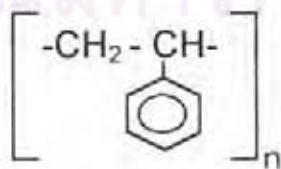
$$\left[-CH_2 - CH- \bigcirc \right]_n$$

Figure 3.1 Polystyrene

Because of the chain stiffening effect of the benzene ring the T_g's of commercial materials are in the range 90 - 100 ^oC and the isotactic polymers have similar values (approx. 100 ^oC). A consequence of this T_g value plus the amorphous nature of the polymer is that we have a material that is hard and transparent at room temperature.

The pure hydrocarbon nature of polystyrene gives it excellent electrical insulation characteristics, as a result of both the fundamentally good characteristics of the material and to the low water absorption of such a hydrocarbon polymer. The insulation characteristics are therefore well maintained in humid conditions.

Polystyrene is a hard, rigid, transparent thermoplastic which emits a characteristic metallic ring when dropped. It is free from odour and taste, burns with a sooty flame and has a low specific gravity of 1.054. Because of its low cost, good electric insulation properties, colorability and reasonable chemical resistance it is widely used as an injection molding and vacuum forming material. Additionally the low thermal conductivity has been made use of in polystyrene foam used for thermal insulation. The principal limitations of the polymer are its brittleness, inability to withstand the temperature of boiling water and its mediocre oil resistance.

The many applications of polystyrene include injection molded products, such as low-cost disposable serviceware, cabinets, toys, etc. Extruded products include finished goods, such as profiles or pipes as well as sheets which are subsequently thermoformed into small or large objects. Polystyrene is also widely used as a cellular material for insulation or packing applications.

3.2 Colorants for plastics

The use of colorants makes it possible to produce a great variety of materials in colors varying from pastels to deep hues, as well as the varicolors and

marblelike shades. Broadly speaking, there are two types of colorants used in plastics, namely, dyes and pigments, both organic and inorganic, the essential difference between them being that of solubility. Dyes are fairly soluble in plastics, whereas pigments, being insoluble, are dispersed throughout the mass.

3.2.1 Pigments

Pigments have average particle sizes in the range of 0.01-1 μm, which differ from product to product and during production are capable of being influenced within certain limits. In the definition of pigment particles, a distinction is made between primary particles or single particles, aggregates and agglomerates (see Figure 3.2).

Because of their extremely small particle size , *primary particles* such as those usually obtained during production, exhibit a pronounced tendency to combine. This massing together in a single plane results in the primary particles forming *aggregates*, which thus possess a smaller surface than that corresponding to the sum of the surfaces of their primary particles. The massing together of primary particles and/or aggregates at their corners and edges results in the formation of *agglomerates*, the total surface of which deviates only slightly from the sum of the individual surfaces. Their size and size distribution are responsible for the coloristic properties.
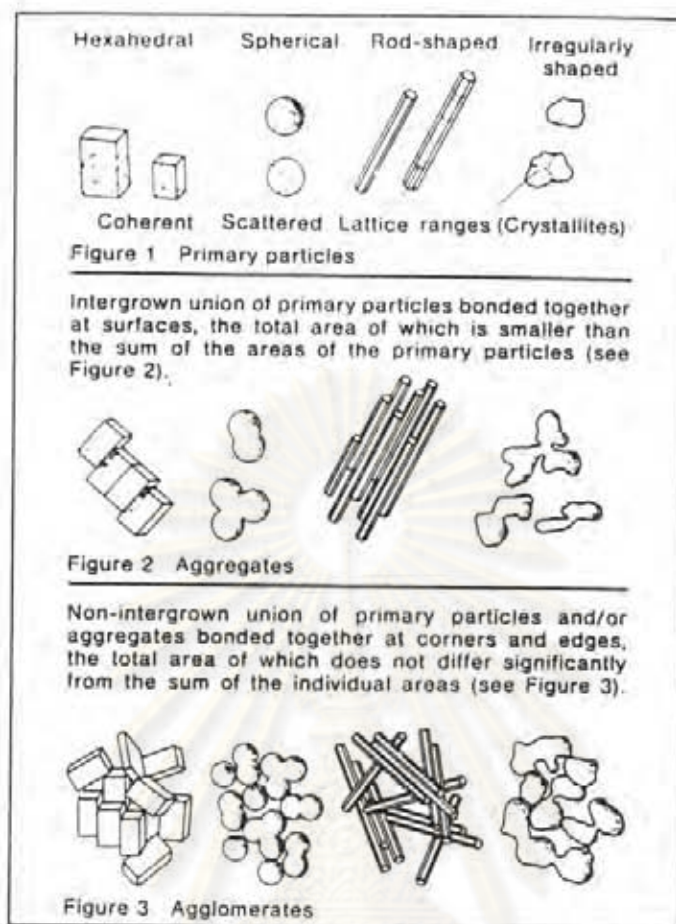
Hexahedral   Spherical   Rod-shaped   Irregularly
                                          shaped

Coherent   Scattered   Lattice ranges (Crystallites)
Figure 1   Primary particles

Intergrown union of primary particles bonded together
at surfaces, the total area of which is smaller than
the sum of the areas of the primary particles (see
Figure 2).

Figure 2   Aggregates

Non-intergrown union of primary particles and/or
aggregates bonded together at corners and edges,
the total area of which does not differ significantly
from the sum of the individual areas (see Figure 3).

Figure 3   Agglomerates

Figure 3.2 Elements of a pigment

Pigments are classified by their chemical nature as being inorganic or organic. Generally, organic pigments are complex chemical compounds that contain one or more benzene structures. Inorganic pigments are usually metallic oxides.

Pigmented plastics are opaque and light-sensitive, fading on the surface and obscuring the unchanged pigment beneath. Coloring with pigments is more difficult, particularly with organic pigment. Incorporating pigment into the various resins often requires special technology and equipment.

A pigment first of all must meet given end-use requirements, such as lightfastness, transparency or opacity, brilliance, or color, down to the specific shade. It also must disperse well. The dispersion of a pigment is a process by which pigment particles are "wetted" down by the resin in the liquid or molten stage.

How well a pigment disperses depends on the temperature at which the two materials are mixed, the particle size of the pigment, and the molecular weight of the polymer. The mixing time and equipment are very important. Often the undispersed particles will detrimentally affect the physical properties of the plastic. It is possible to compensate for loss of color strength by using more pigment, but this substantially increases cost.

Pigments can be only broadly classified in terms of dispersibility. Large-particle-size materials such as titanium whites are easiest to handle. Generally, inorganic pigments have fairly large particle sizes, but only a few are as easy to work with as titanium pigments.

By contrast, organic pigments are usually the most difficult to disperse. Many can be dry-blended with resins and extruded or injection-molded on conventional equipment, but the preparation prior to the dry blending often requires skill. The blending sequence as well as the expert use of dispersing aids can be important. Some organic pigments are so difficult to disperse that only the most efficient equipment can be effective. Organic pigments are very light and fluffy and carry electrostatic charges, all of which makes dry blending very difficult.

In the present study, iron oxide was used as inorganic pigment and carbon black was used as organic pigment.

3.2.1.1 Iron oxide

Iron oxide pigments, inorganic, were selected for use in the present study. Generally, they are divided into those of synthetic and natural origins. There are several yellow, brown, red, and black oxides. As a class, they provide inexpensive but dull, lightfast, chemically resistant, non-toxic colors. The natural products are known as ocher, sienna, umber, hematite, and limonite. They include varying amounts of several impurities; in particular, the umber contains manganese.

The synthetic iron oxides are of much higher purity and have less variation in composition. The red iron oxide, Fe_2O_3, has excellent bleed, chemical, heat, and light resistances and is non-toxic. The yellow hydrate, $Fe_2O_3 \cdot x$ H_2O, is useful up to 175 $^{\circ}C$, where it loses water and becomes red. Both of these pigments protect resins by screening ultraviolet light. The brown oxide, a mixture of ferrous and ferric oxides, $(FeO)_x(Fe_2O_3)_y$, is useful for producing wood-grain effects in plastics. There are also two mixed oxides, $ZnO \cdot Fe_2O_3$, and $MgO \cdot Fe_2O_3$, that are stable, non-toxic tans.

The natural iron oxides are recommended for use in cellulosics and phenolics, the synthetics for cellulosics, polyethylene, polystyrene, flexible vinyls, and all thermosets.

3.2.1.2 Carbon black

Carbon black is the name given to a wide variety of finely divided black pigments composed mainly of elemental carbon. Such pigments are usually produced by pyrolysis of hydrocarbon gases or oils. Carbon black is widely used as a reinforcing and coloring agent in compounding rubber, inks, paints, plastics, paper, protective coatings, and electrically conducting applications.

Carbon black is used in a wide range of thermoplastic and thermoset resins. Generally the uses for carbon black in plastics involve one or more of the following applications:

- Stabilization against ultraviolet light

- Reinforcement of mechanical properties

- Coloring and opacifying

- Cost-reduction, as a filler

- Electrical conductivity

- Thermal conductivity

Carbon black is produced commercially by the decomposition of hydrocarbons in the vapor phase, using quite complex flame technology. Five basic processes are associated with the production of traditional carbon blacks. They are, in order of importance, the furnace, thermal, acetylene, lampblack and channel black processes, with average particle sizes varying between 10-100 nanometres. While color intensity and tinting strength are determined mainly by the particle size, the surface characteristics and structure of the carbon blacks are also important for other technical applications.

Many specialty grades of carbon black are available as powders or beads (also referred to as pellets), which is a great advantage for the varied applications in the plastics industry. The choice often depends on the resin form, the type of concentrate or compounding equipment available, and the technique that will be used for incorporation of the carbon black. Usually they are first converted to a plastic concentrate. Concentrates or master batches range from 20 to 60 % carbon loading and enable a higher level of dispersion of the carbon black to be achieved. A number of companies specialize in mixing carbon black to customer formulations, and many also provide a variety of proprietary products designed for specific applications containing high loadings of carbon black in a number of the more common polymers and elastomers. These concentrates can be easily let-down or compounded, often in less intensive mixers such as extruders and screw preplasticizing injection-molding machines. The latter method avoids contamination and dusting problems in the end-product manufacturer's plant, and assures high quality levels. Because conductive products usually contain 15 or 40 % carbon black, concentrates generally are not used. In some cases where the resin system is in powder form (such as PVC), the carbon black is added to the final 1 to 3 % level, and either dry-blended in the powder form or premixed in a high-intensity mixer.

3.2.2 Dyes

Soluble dyes are the easiest to use. As the resin liquefies in an extruder or an injection molding machine, the dye dissolves in the resin. All dyes are transparent. Most have relatively poor light fastness and limited heat stability, but give bright shades in transparency is desired.

3.2.3 Coloration criteria of styrenic polymers

In the past, the coloration of unmodified (crystal) polystyrene (PS) and styrenic copolymers was largely carried out by the resin manufacturer. This took place almost exclusively in the melt with single pigments using a kneader or extruder. Because of technical problems, and particularly to improve the quality of coloration in finished articles, the processor carrying out his own coloration at the present time gives preference to pigment concentrates, occasionally in liquid form. Direct coloration using readily dispersible colorants in powdered form is, of course, also possible. The latter are dry-blended with polystyrene pellets in a mixer at room temperature. A maximum of 0.5 % of an adhesion promoter or dispersing agent is added where necessary, and the mixture is processed under relatively high back pressure on screw injection molding machines with good mixing action, or on extruders.

When colorants are dry-blended with polystyrene, account must be taken of the fact that crystal polystyrene is a very hard and brittle resin. With pigments which are highly sensitive to abrasion, the sharp cutting edges and corners of the pellets can cause shifts in shade. A coloristic change due to metal abrasion during mixing in metal drums is also possible. Plastics-coated mixer walls or blending in plastics vessels (tumblers) are suitable alternatives.
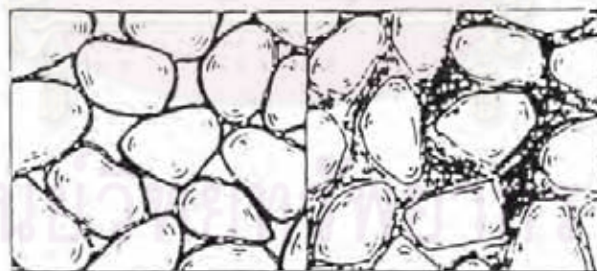
3.3 Kneading

Definition and significance of kneading

Forming of powder must be preceded by kneading in the presence of a liquid binder that serves to bond the particles together. The structure of resulting formings may be classified into two types, as shown in Fig 3.3: film type and matrix type. Kneading is a pretreatment for powder forming process and defined as follows:

1. Film type: thin coating of the surface of each particle with the binder

2. Matrix type: coating of the surface of each particle with a large amount of binder, or dispersing the powder in the matrix of the binder.

Since a binder is generally more expensive than powder, its applied amount should be reduced to a minimum, and the process of kneading is of great significance to this end.

Film Type   Matrix Type

Figure 3.3 Structure of resulting formings

Major Factors that influence kneading

The major factors that influence kneading may be divided into two groups: those related to kneading materials and kneader. The former includes the viscosity of the binder and the wettability between powder and binder. The lower the binder

viscosity and the higher the wettability, the easier will be the coating of the powder surface with the binder. The latter includes the kneading force and speed of kneaders. The kneading force implies the coating or dispersing power of a kneader; hence a kneader with a high kneading force is capable of satisfactory coating or dispersing powder even with a binder of high viscosity or low wettability. It is advisable that a kneader of proper kneading force be selected on the basis of the properties of kneading materials. The kneading speed is a measure of the time until the kneader completes kneading. Kneaders of higher keading speed are preferable.

Type of kneaders and their selection

Among a variety of powder technologies, kneading is an art for which theoretical analysis is least advanced and past experience is important for successful operation. Therefore, it is common practice to select proper kneaders by repeated experiments and intuitive experience, not by theoretical consideration. The best way would be to select as few kneader candidates as possible by considering the kneading material factors and by using the checklist below, and the next step is to determine the proper one after testing actual kneaders exhibited by manufacturers.

1. Even coating of the powder surface with the binder
2. Proper kneading force
3. Rapid kneading
4. No need to premix
5. Little tendency for mechanical parts to wear or corrode
6. Ease of cleaning
7. Good afterservicing and ready supply of mechanical parts

3.4 Compounding

Few resins are useful in their natural form; so they are mixed with other materials to improve and enhance their properties and thereby make them more useful for a variety of applications. The process by which ingredients are intimately melt-mixed together into as nearly a homogeneous mass as is possible is known as compounding. Because of the nature of both the resin and the other ingredients, compounding requires a wide range of mixes-dry powders, slurries, pastes, doughy consistencies, for example, and a corresponding range of mixing operations.

The task of mixing becomes one of changing the original distribution of two or more nonrandom or segregated masses, so that an acceptable probability distribution of one mass throughout the other(s) is achieved. Thus the problem becomes one of deforming or redistributing masses in order to achieve this desired probability distribution, in the absence of diffusion or other random molecular motions. A problem arises if the ultimate particles are not independent of one another, but instead exert interparticulate forces leading to particle agglomerations. Then, external force must be exerted on such agglomerates to allow them to mix. Dealing with these forces, or stresses, is at the heart of dispersion processes.

In mixing and dispersing processes involving thermoplastic melts, the thermoplastic material is regarded as essentially a fluid subjected only to laminar flow, capable of being deformed. Thus, the problem of mixing in thermoplastics is that of subjecting such materials to laminar shear deformations in such a manner that an initially nonrandom distribution of ingredients approaches some arbitrary scale of randomness. Mixing usually is complicated by the fact that ingredients do exhibit interparticulate forces,so that stresses accompanying the deformation must be considered, as well as the deformation process itself.

Strictly speaking, compounding involves the fusion of different materials into a homogeneous mass that is uniform in composition and structure. The actions in this type of mixing consist of smearing, folding, stretching, wiping, compressing, and shearing. However, component materials may be dry-blended either in preparation for compounding or for direct product fabrication. The major types of plastics compounding equipment in current use are as follows:

Miscellaneous Batch Mixers

In most instances, the polymer feedstock to a compounding operation is in particulate form, as are most of the additives. Compounded polymer grades are frequently preblended by adding the additives to the polymer or mixing the additives to form a package. When small amounts of a number of additives are required, premixing is an inexpensive route to the final formulation. Mixers used for preblending are predominantly batch mixers, usually for particulates. Preblending usually achieves distributive mixing only. These mixers include: drum tumbler, double-cone blender, V-blender, and ribbon blender as shown in Figure 3.4.

Intensive Dry Mixers

Intensive dry mixers are used for dry-blending powdered resins, such as PVC, with plasticizers and other additives. A typical mixer consists essentially of a high-speed propeller-like impeller located at the bottom of a container (Figure3.4).

Internal Intensive Batch Mixers

Essentially, internal mixers consist of cylindrical chambers of shells within which materials to be mixed are deformed by rotating blades or rotors. The most well-known mixer is the Banbury mixer, which consists of two spiral shafts which rotate about fixed centers in a counterrotating mode (see Figure 3.5).
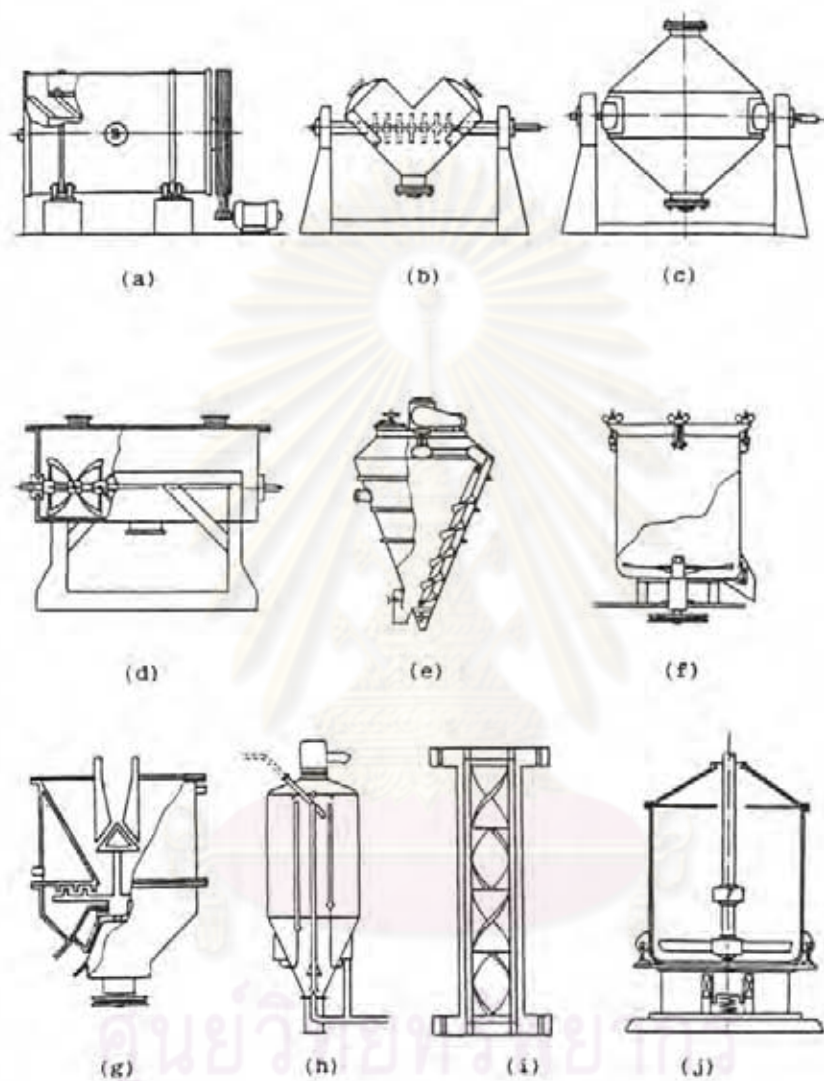
Figure 3.4 Typical examples of mixers

(a) Horizontal cylinder (b) V-blender (c) Double cones (d) Ribbon

(e) Screw in cone (f) High speed (g) Rotating disk (h) Moving or

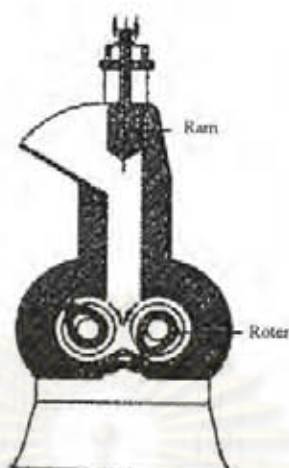fluidized bed (l) Motionless (j) Vibration and mechanical agitation

Figure 3.5 The Banbury mixer

Two-Roll Mills

The two-roll mill consists of two oppersiterotating parallel rollers placed close to one an other with the roll axes lying in a horizontal plane (Figure 3.6), so that a relatively small space or nip between the cylindrical surfaces exists. Material reaching the nip is deformed by friction forces between itself and the rollers and made to flow through the nip in the direction of roll motion.
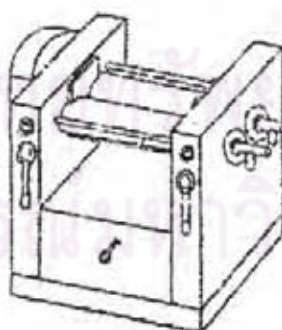

Figure 3.6 The roll-mill batch mixer

Single-Screw Extruders

Although developed to form thermoplastics, the single-screw extruder (Figure 3.7) also functions as a mixing device because it subjects materials to

laminar-flow deformation. Thus, although the extruder is not primarily used as a mixer, it is frequently used to add ingredients to a resin during melt extrusion and thereby to take advantage of their inherent mixing action. It is quite common for colorants to be added to exturded products in this way. The barrel is heated, both the colorant and the resin, fed as solid particulates, melts. The melt is mixed by circulating in the channel. The melt is then pumped from the extruder as compounded polymer.

The amount of mixing a given volume of resin receives may be expressed in terms of the total amount of shear to which the resin is exposed. It is the product of share rate and the extruder residence time, and is a measure of the relative displacement of one particle with respect to its neighbor.
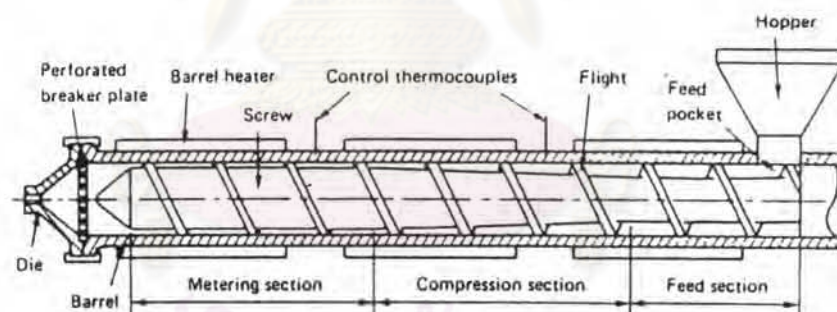

Figure 3.7 Single-screw extruder

The applicability of single-screw extruders to compounding has been enhanced by some innovative ideas. Additives, primarily glass fiber, could be introduced downstream through the extruder barrel into the melt using a screw-type feed perpendicular to the screw axis. This ensures that the glass fiber is added directly to the melt. There is, therefore, less wear to the screw and barrel and less loss of glass fiber.

Twin-screw extruder

In twin-screw extruders, two screws are arranged side by side (Figure 3.8). One design incorporates co-rotating screws that are intermeshing and self-wiping. Because the screws rotate in the same direction, material moves helically along the inside barrel wall in a figure-8 path from the feed section to the discharge point.

Screw configurations are used to vary conveying efficiency, throughput rate, the degree of filling, and pressure buildup. Screws with reversed flights are used to generate localized high pressure. Hydraulically operated dynamic valves between barrel sections can be used to allow pressure variations during operation. Staggered stepped screws provide intensive transversal mixing and kneading effects are obtained by suitable screw design.

The residence time is determined by the barrel length, screw lead, screw speed, and throughput rate. The residence time depends on the process and operating conditions. Residence time distribution may be influenced by changing the screw geometry, by which the residence time distribution can be widened to handle considerable longitudinal mixing.

With counter-rotating screws, screw fights carry material by friction in such a direction that all of it is forced toward the point where the two screws meet, there forming a bank of material similar to that of a two-roll mill, although some material slips through the gap between the two screws. As with the two-roll mill, the theory is to feed material through the nip from the bank on top of the nip gradually and statistically, in order that each particle be processed equally over a period of time.

In co-rotating twin screws, one screw transports the material around up to the point of intermeshing, where, because of the existence of two opposing and equal velocity gradients, a great majority of the material is transferred from one

screw to the other along the entire barrel length in the figure-8 path mentioned earlier. Because the figure-8 path is relatively long, the chances of controlling the melt temperature are much better with this design.

Self-cleaning screws, aside from the obvious advantage of facilitating color change, provide control over residence time distribution. Control of residence time also is of great importance for heat-sensitive resins and pigments, or for operating at higher processing temperatures. A short and uniform residence time is essential to minimize heat and shear history, and, thereby, to maximum quality.
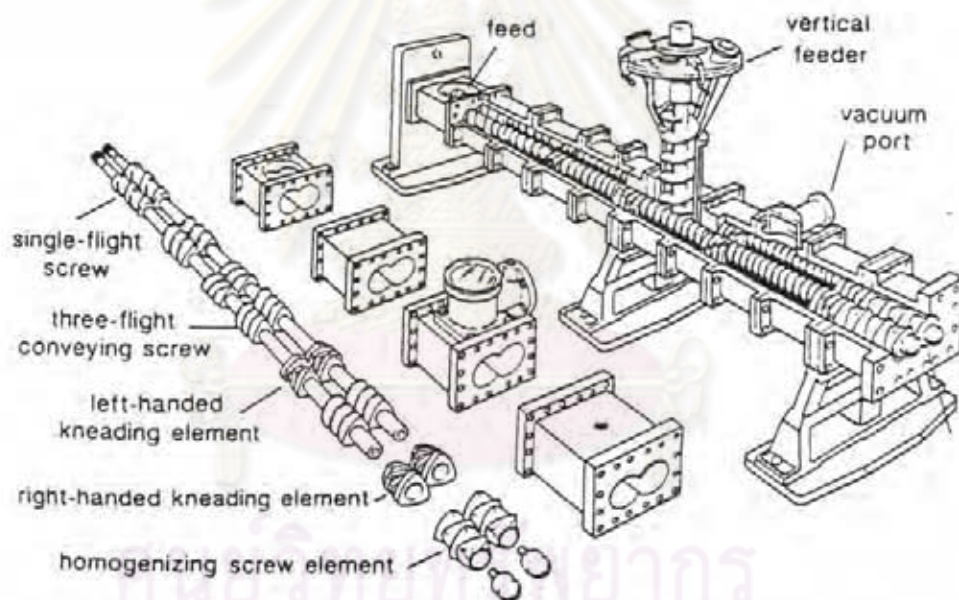

Figure 3.8 Twin-screw extruder

Continuous Kneader

This mixer is an adaptation of a sigma-blade mixer for continuous operation. Each two pairs of blades establish a mixing zone, the first pair pushing materials toward the discharge end of the trough and the second pair pushing them back. Forwarding to the next zone is by variation in rotor speed. Cored blades supplement the heat-transfer area of the jacketed trough.
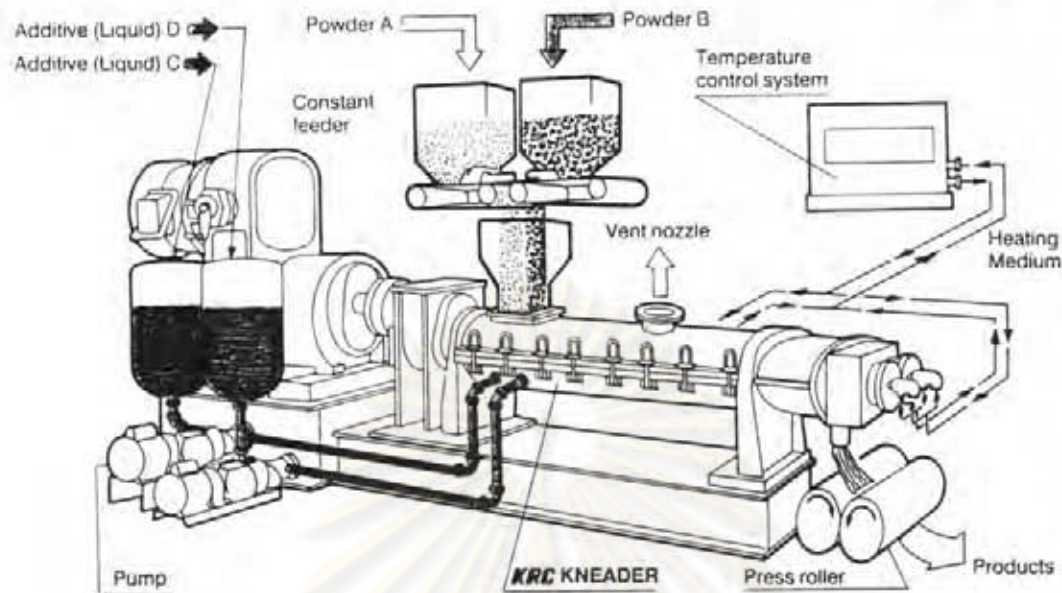
Figure 3.9 Flow sheet of continuous kneading

3.5 Dispersion of pigments in plastics

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 mixture between carrier and pigment. It is essential to every dispersion regardless of quality. At a minimum, it requires that pigment and carrier be sufficiently well mixed and have sufficient affinity for each other so they would not separate when further work is applied to the system. The mutual affinity, compatibility, or wettability of two materials can be increased through a change in the surface characteristics of either or both, by use of surfactants. Pigments, being of many different chemical types with different surface characteristics, 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 pigments 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 pigment aggregates and agglomerates to primary pigment particle size. Studies of the processes which mix pigments 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 polymer, which rupture the agglomerates. When these stresses (the magnitudes of which are determined by the viscosity of the polymer 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 required to overcome the adhesive strength of the particles, it would not be dispersed. Because the consistency and tack of the polymer influence the effectiveness with which the mechanical energy could be transmitted to the particles, predispersion in a medium other than the base polymer is often considered.

The bond energies between primary particles in pigment 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 pigment might yield better results than another at a low shearing stress but be inferior at a higher shearing stress. Ratings at several levels of stress

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 pigment-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 plastics/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 a pigment aggregate unless a bond exists between the pigment 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 area and microscopic interstitial pores. Such pigments often require extended dispersion cycles to achieve desired results.

While many attempts have been made to study pigment dispersion, most have been restricted to the fields of paint and printing ink, and few are related to the plastics media. Irrespective of the medium used, dispersion levels have been shown to improve with increasing the power or the speed of mixing, but they might also be accomplished with longer mixing times.

Dispersion is an exponential disintegration process analogous to radioactive decay. The amount of dispersion taking place at any time (i.e., the rate of dispersion) depends upon the number of dispersible particles present, their strength, and the maximum shear stress. If all particles are of equal strength, the

rate of dispersion is independent of time, although the total change in dispersion is not.

The total change in dispersion, and hence the ultimate coloration developed, is dependent upon the energy of the mixing process. As the time of mixing is increased, the value for the total change approaches, asymptotically, a maximum level corresponding to that achieved by mixing for an infinitely long time at that level of shear. But long processing times do not compensate for a lack of intensity of shear, and no matter how long the process is extended, low shear levels would not generate good color development. This relationship has been observed with many different pigments.

Dispersion becomes progressively more difficult as particle size decreases. At some threshold size, any further increases in dispersion ceases completely. As yet there is no means available by which the strength of these small pigment particles might be measured, and therefore no definite idea might be formed of the size of the smallest dispersible particle or of the way in which this changes with the ambient rate of shear.

Since dispersibility varies with agglomerate size, it is to be expected that each size would disperse at a different rate. The observed rate of dispersion in a population of particles containing a range of different sizes would thus be given by the average of all the individual rates of dispersion. Since the rate of dispersion for small particles would contribute very little to the overall observed rate during the early stages of mixing, the early rate of dispersion would depend on the number of large particles. As the mixing cycle is extended and the large particles disappear, the small particles would become more dominant, and the rate of dispersion would fall. This might or might not be noticeable, depending upon the level of shear and the difference in dispersibility between the large and small particles.

As might be expected, the level of dispersion achieved with any mixing process depends upon the energy required to disperse the agglomerates and the ability of the process to supply that energy. The two aspects of this relation might be examined separately.

The mixer used for a compounding operation would, by the nature of its design, determine the maximum level of shear which might be developed within any given polymer at any operating temperature. It is well-established, for example, in the plastics compounding industry, that every mill developed a specific energy which in turn limits the level of dispersion finally achieved.

Design would also control the residence time (that is, the time for which the agglomerates are exposed to shear) as well as the proportion of that time during which the agglomerates are exposed to high rates of shear. Time must be allowed, in any mixing process but especially in batch mixing, to ensure that all the agglomerates which are present pass through the zone of the highest shear. Other variables limit the shear developed during mixing; these include the operating temperature, the nature of the polymer, and the mixer speed. Higher speeds raise the energy input as well as pass material through the zone of maximum intensity more frequently. Thus, more agglomerates are dispersed more quickly.

The theoretical discussion on dispersion mixing may be summarized as follows:

1. Dispersion is a combined effect of size reduction and wetting-out of pigment particles by the carrier.

2. High shear promotes dispersion.

3. There is some threshold stress below which no dispersion would occur.

4. Larger agglomerates would disperse more easily than the small ones in the early stage of dispersion.

5. The total change at any time in a dispersion process is dependent upon the time of mixing.

6. The ultimate level of dispersion achieved depends upon the maximum shear available in the mixer. The higher this rate of shear, the greater the change in dispersion.

7. The maximum level of dispersion is approached asymptotically as mixing proceeds. Evaluation of dispersibility of pigments in plastics shows that dispersion is a first-order process.

8. Pigments differ considerably in their response to shear: in general, inorganic pigments disperse more easily than organic pigments.

3.6 Dispersion methods

The basic dispersion processes for pigment-plastic systems are:

Dry Blend Dispersion   Dispersion by dry blending alone occurs largely by impact and attrition. Except when followed by other dispersion processes, little opportunity exists in later processing to achieve the intimate wetting needed for some critical applications. Nevertheless, technique and equipment have been developed that permit production of good-quality dispersion by this method. The most important of these are non-fluxing high-intensity mixers and use of particulate resins in pigment-resin co-blending.

The need for equipment that would impart high velocity or impact to pigment particles is obvious, since aggregates and agglomerates can be fragmented only by exceeding the energy level with which they are bound. One common method is ball-milling the pigment with the plastic powder at low temperatures. In general, dry-blend dispersion has been more effective at low-pigment loading than at high

loading primarily because of the caking tendencies of many pigments and extenders.

Pigments vary not only in the energy required to break up aggregates, but also in their susceptibility to over-grinding. Fracture of the primary particle size (as happens with lead chromates and cadmiums) or compaction into aggregates larger than are initially present (many organics) are the two most frequent results of over-grinding, both of which produce large and undesired changes in color and often in performance. Some pigments have also been known to change crystalline phase, with an accompanying sharp color change, when dry blended too vigorously with certain resins. These changes are, of course, in addition to the commonly encountered problem of discoloration caused by abrasion of the equipment during grinding.

The value of using particulate resins in preference to larger granules or pellets seems to lie in the significantly improved initial wetting obtained. The importance of this should not be underestimated, even if used only in preparation for melt shear dispersion. Experience shows that pigments are more easily and completely incorporated into a resin when they are attached to the resin surface prior to melting. Finely divided resin not only provides more surface for coating, which permits working at higher pigment concentrations, but also puts the pigment in more complete, intimate contact with the total resin mass so that shear is transmitted immediately and more effectively in the vital initial stages of fluxing. In other words, no large localized regions of high-resin and high-pigment content exist alongside each other. If they do, inherent differences in consistency and melting temperature would undermine the quality of mixing obtained.

It might seem illogical that a resin size that would significantly reduce impact stress when hitting a pigment particle would still result in higher-quality dispersion. However, this attests to the very real value of initial wetting to aid both size

reduction (by shear) and more complete wetting in latter stages. Of course, the pigment must adhere to the resin well enough to survive intermediate handling. Additives that would render the resin surface more wettable are often used to improve this bond, and use of resins with a highly porous surface has been suggested. Methods of increasing electrostatic attraction between pigment and resin might also be considered, since this appears to be the basis for good adhesion in some systems.

Melt Shear Dispersion As its name implied, melt shear processes depend on transmission of high shear through resin to achieve dispersion. This is the most-used method of pigment dispersion in plastics. Melt-dispersion conditions are usually best at, or very near, the softening point of the system because of the high-internal shear that can be developed at this point. At higher temperatures the process becomes more one of mixing than dispersion because of the greater fluidity. Opportunities might be available in the more complex formulations to withhold one or more ingredients (lubricant, plasticizer, low-tack oil) to improve the working consistency of the compound for dispersion; they could be added at the completion of dispersion. Similarly, highly efficient additives or extenders that increase consistency through surface absorption has been helpful. In line with this approach, dispersion at high-pigment loadings, i.e., concentrated levels, is the very essence of the well-known and highly regarded dispersion process used to provide high-quality dispersions to the vinyl, lacquer and cellulose acetate fiber industries.

As mentioned earlier, the effectiveness of shear transmission to a pigment particle through an intermediate fluid film would depend on: the quality with which the fluid wets the pigment and equipment surfaces; the viscosity of the system under actual dispersion conditions; and the internal cohesive strength of the fluid (referred to in some industries as its tack). Each of these, then, suggests directions that could be taken to improve dispersion. Tack is an inherent characteristic of the

resin; the only latitude in dealing with it is to either modify the resin or select an alternate, compatible carrier as a dispersing medium if tack severely limited dispersion in the base polymer. Wetting is a function of both the fluid and the surface to be wetted. Again, surface-active agents can often be used to improve wetting or an alternate carrier might be available offering better wetting characteristics. Viscosity is more within the practical means of the compounder to control, but first he needs some basis for determining what level is desired, and also to recognize that viscosity is likely to fluctuate widely during processing of thermoplastics.

All melt dispersion equipment for plastics depends on the utilization of hydraulic shear to break down pigment aggregates. This shear is, of course, directly proportional to the viscosity of the polymer which in turn is directly dependent on the temperature involved. The temperature developed in milling a plastic is a limiting factor in many operations since it reduces the viscosity on which the shear depends.

Three general types of equipment are in use today: two-roll mills, Banbury mixers, and compounding or milling extruders.

Two-roll mills are excellent for producing good pigment dispersion. Through careful temperature regulation of the rolls it is possible to maintain the viscosity of the plastic mass indefinitely, within a desirable range for producing the shear necessary for dispersion.

The Banbury mixer is designed to produce intensive mixing at high viscosities. A relatively high-power input is concentrated on a small volume of material. The result is extremely high shear and rapid temperature build-up. The increase in the temperature results in a pronounced drop in the viscosity of the mass with resultant loss of shear. This is the limiting factor in this equipment, as dispersion must be accomplished very quickly before the mass loses the viscosity

necessary for shear. Since very high-shear rates exist in the early stages of this process, it is possible to do a reasonably good job in the time usually available.

The two-roll mill and the Banbury mixer are both capable of producing good dispersion. It is usually necessary to use the Banbury in conjunction with a two-roll mill; this combination probably produces the best pigment dispersion in plastics, that can be obtained by mechanical means.

The compounding extruder is similar to a two-roll mill in principle, with the important exception that with the extruder the material is in the working area for a limited time. Here again, dispersion is dependent on the development of suitable shear rates. This can be accomplished through proper screw design and temperature control in the compounding zones. Various screw designs are available for compounding. In all cases, fairly close clearance between screw surface and extruder barrel is desirable to generate the shear area so necessary for good pigment dispersion. The screw design should contain a large proportion of metering area. Some areas of the screw are frequently left without flights to further increase the area of minimum clearance between the extruder barrel and the screw. It is possible to do a fairly good job with an extruder, particularly if the pigment and polymer have been subjected to intensive mixing beforehand.

Liquid Dispersion   Liquid-colorant addition to plastics during processing has become firmly established in many resin-fabricating operations, and has a quite exciting projected rate of growth. The advantages of liquid colorants relate directly to better economics and the ability to automate operations. Technological advancements lead to improved product quality. In addition, the concept of colorant addition in a liquid carrier has been expanded to include the simultaneous feeding of many other plastics additives such as blowing agents, antioxidants, UV stabilizers, and lubricants, all in a single operation.

In liquid colorants, the dispersion of pigments is made in a liquid carrier, which might be a plasticizer, polymer solution, low-molecular weight polymer, or a combination of these. Carriers for liquid colorants are selected for compatibility with a wide range of thermoplastic resins and plastisols. In fact, liquid colorants are now available whose carrier systems are compatible with virtually all widely used thermoplastics, including many engineering resins such as polycarbonates, phenylene-oxide-based resins, nylons, polysulfones, and others. This degree of compatibility results from several specific properties of the carrier system, whereby there is a small degree of chemical compatibility that allows the system to bond to the polymer chain. However, the major degree of compatibility is obtained by an emulsification process that produces a high degree of syntactic abilities in the resin matrix. The total effect is to provide a carrier system with a high degree of stability for carrying colorants into a resin without significant effect on the resin's physical properties.

The carrier system for liquid colorants involves other considerations relating to product performance. One characteristic involves the optimization of pigment dispersion in the finished liquid colorant. The technology here consists of mathematically computing the required surfactant blends for a given pigment to permit the maximum amount of solids content with the minimum of residual surfactant in the dispersion. This process is described by the HLB system (hydrophile-lipophile balance) built on the theory that numerical designation can be calculated to reflect the type of behavior expected from a surfactant system. Then, coupled with the empirically derived and established requirements of known colorants, pigments can be dispersed for their optimum effect while maintaining other important performance characteristics of the overall liquid-colorant dispersion.

The approach to pigment dispersion in a universal carrier has led to the ability to create liquid colorant dispersions to accommodate virtually all colorants

used by the plastics industry. Hence, a formulator can meet the highest criteria for coloring requirements, including those of the FDA and USDA.

The greater variety of dispersion processes are available for liquid systems because they are easier to handle and offer greater latitude on formulation. The mode of energy transfer (i.e., impact, attrition, or shear), still dictates the level of fluidity needed. Liquid pigment dispersion technology has borrowed a lot from paint technology. All those technological processes which are employed by the paint industry are important in the preparation of liquid dispersions. Shear processes are common, as they perform best at high viscosity.

At high loadings, particularly, pigments can have rather pronounced non-Newtonian effects on viscosity so that viscosity measurement on a millbase at rest might give little insight into its actual consistency during milling. Furthermore, viscosities of millbases containing high-surface area pigments tend to increase sharply during dispersion as the pigment surface is wetted, so that viscosity adjustment might be required during the grinding to maintain proper working consistency.

The quality of initial wetting in liquid dispersion is easily measured by its mix-in time, i.e., the time required to form a coherent mass, or, in the case of a three-roll mill dispersion, the time needed to eliminate tailings and separation. Surfactants can be particularly effective at this stage of dispersion. Progress in particle-size reduction is generally followed by fineness or texture measurement on a grindometer scale; however, the compounder is again reminded that this measurement does not necessarily correlate with development of other dispersion attributes of importance, e.g., color, opacity, haze, etc., which involve particle sizes that can not be measured by this method.

Principles of millbase formulation and equipment operation to achieve optimum result in liquid shear dispersion are much the same as already described for melt shear processes.

Rheological factors are paramount in determining the pigment loading of a liquid dispersion. The limiting factor in this connection becomes the viscosity that allows for proper incorporation into plastics, with the mixing equipment at hand. For plastisols, the optimum viscosity is a viscosity similar to that of the plastisol. For incorporation in thermoplastics, high viscosities can be tolerated.

In any discussion of viscosity, one can not overlook the effect of the surface treatment on the pigment. It is different for each pigment manufacturer and can result in dispersions of different viscosities. Resistance to flow of liquid dispersions might sometimes become a problem. In this case, a reduction of pigment concentration generally alleviates the problem. "Short" and "buttery" dispersions are extremely difficult to incorporate into a plastisol. This problem arises because of some physical interaction of pigment with the dispersion liquid-probably a swelling of pigment particles involved. Benzidine pigments are notorious for this.

The plastics industry is gradually turning to the use of liquid dispersions. Liquid pigment dispersions are introduced some years ago, with disastrous results. One reason is that the wrong dispersion media are chosen; also, the early colorants cause plating out on the screw. Another reason the liquid-colorant concept has developed such a bad reputation is that one of the major areas of interest, polyolefins, is completely neglected in the early days.

Liquid dispersions utilize conventional high-performance organic and inorganic pigments dispersed in a liquid vehicle system which is essentially nonvolatile at normal molding temperature up to 400°C. Like solid dispersions, the vehicle becomes an integral part of the resin matrix. The vehicle is capable of carrying high loadings, in the range of 60 to 70% pigments. Because of the nature

of liquids, the dispersion characteristic of pigments in liquid systems is much more important than in solid-type systems.

Some concern about the possible migration and exudation of the liquid vehicle on the surface of the pigmented plastic part still exist among the plastics technologists. Carrier migration has been, in fact, a source of trouble. New liquid dispersions are reported to be free from this defect and the recent experience of the industry has confirmed these claims. The coloring costs based on using liquid dispersions are competitive with the costs of dry dispersions.

In practice, a combination of these processes is often employed to take advantage of the merits of each. For example, intensive dry blending before melted dispersing could improve dispersion quality as well as reduce overall cost, and predispersion in plasticizer is often the least expensive means of obtaining high-quality dispersion of some colorants in vinyls. The development of dispersion procedures by any of these processes has been largely empirical, depending heavily on the past experience a formulator has had with pigments, dispersing equipment, and resin systems. However, application of the dispersion theory should suggest ways in which these procedures can be improved.

3.7 Evaluation methods of dispersibility

The quantitative evaluation of the dispersibility has a few of methods that could be summarized as follows :

3.7.1 ASTM D2663

ASTM D2663 was the standard test method for carbon-black dispersion in rubber. This method is carried out by measuring the aggregate percentage of the areas covered by pigment particles and agglomerates in

microtomed sections of the compound material. According to this method, the compounded rubber is microtomed into sections sufficiently thin to permit observation of the carbon agglomerates by transmitted light, with the aid of a light microscope. The total cross-sectional area of all agglomerates 5 μm. in diameter or larger was counted, and from the known content of carbon black in the stock, the percentage of carbon black below the 5-μm size was calculated. The percentage of carbon black that has been dispersed below the 5-μm agglomerate size, is calculated as follows:

$$\text{Dispersion (\%)} = 100 - SU/L \qquad (3.1)$$

where

    U = total number of graticule squares that are at least half
         filled with carbon black

    S = area swelling factor from the action of the solvent
         used to uncurl the sections

    L = volume percentage of carbon black in the compound.

3.7.2 BS 2782 : Part 8 : Methods 823A and 823 B

These methods describe procedures for assessing the carbon black dispersion in polyethylene using a microscope.

1) Method 823A

Method 823A is primarily intended for use with polyethylene compounds but may be used for extrusions and moldings if so specified.

A small sample of the material (approximate mass 0.2 g) is squeezed into a thin layer 20 μm to 30 μm thick between two microscope slides heated to either 170 °C to 210 °C or a higher temperature if specified in the material

specification. The appearance of the layer is then examined by transmitted light at a magnification of X100 against standard microphotographs. Scan the whole of each specimen and compare the worst field of view of each with the standard microphotographs numbered 1 to 7 (1 best; 7 worst). Make the comparison with respect to the number and size of agglomerates, taking into consideration all black particles in the field of view. Assign to each of the six specimens a numerical rating corresponding to the number of the microphotograph equivalent to the worst field of view of each specimen.

Examine the six pressed specimens for uniformity of appearance with respect to smears and streaks by comparing the worst field of view for each specimen with standard microphotograph.

2) Method 823B

Method 823B is intended for use with polyethylene extrusions or moldings only.

A microtome section of the material, 10 μm to 20 μm thick, is examined as for Method 823A.

3.7.3 The fractal analysis method

The fractal analysis method represents another group of quantitative methods to evaluate the extent of pigment 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 (Sirikalaya, 1994). This means that the shape of a fractal has self-similarity and a 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

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 to fractal dimension is straight-forward. A D-dimensional self-similar object can be divided in N smaller 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 3.3, its fractal or similarity dimension is given by:

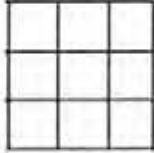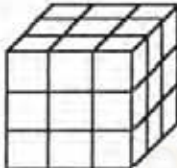$$D = \frac{\log(N)}{\log(1/r)} = -\frac{\log(N)}{\log(r)}$$ (3.2)

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 had fractional dimension between one and two (or between two and three). It could be shown that an extremely irregular shape might be treated as a fractal, for example, the coastline (shoreline) of a country.

Let $N(r)$ be the counted number of subsections (mini squares of side r) containing at least one small part of a fractal when the representative length of each subsection was r, $r = 1/n$ (n = number of division to similarity), the so-called similarity ratio.

For the fractal system, the following equation holds:

$$N(r) = (\text{Similarity ratio})^{-D} = (r)^{-D}$$ (3.3)

Table 3.3 Scaling law for fractional dimension (Sirikalaya, 1994)

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	$1/27^{(1/3)} = 1/3$	$27 = 3^3$

Thus the fractal dimension, D, is defined by :

$$D = -\frac{\log N(r)}{\log r} \qquad (3.4)$$

1) Fractal analysis of shape of pore opening

In the fractal analysis of pore shape (Sirikalaya, 1994), the cut specimens of the porous material (refractory) of interest were micro-photographed using a reflecting microscope. An illustration of the count N(r) versus the similarity ratio r is shown in Figure 3.10.

n = 1   n = 2   n = 4

r = 1   r = 1/2   r = 1/4

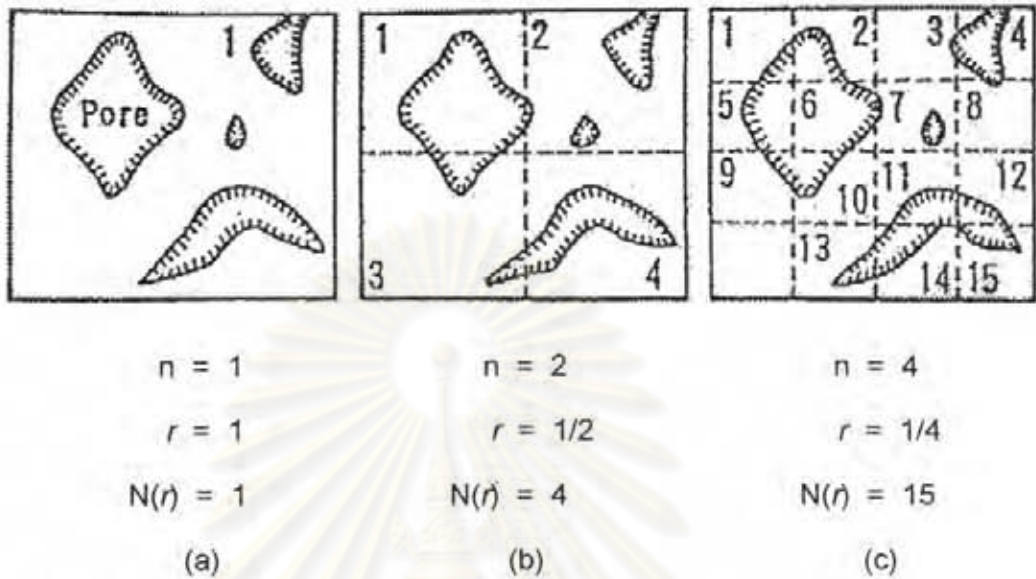N(r) = 1   N(r) = 4   N(r) = 15

(a)   (b)   (c)

Figure 3.10 Determination of fractal dimension (Sirikalaya, 1994)

The observed relationship between N(r) and r was plotted on the log-log scale, and the fractal dimension was calculated from the slope of the convergent straight lines in Figure 3.11.
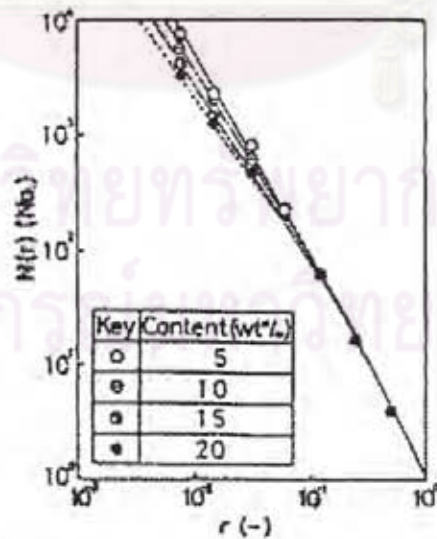

Figure 3.11 Example of fractal dimension determination (Sirikalaya, 1994)

2) Fractal analysis of dispersion state

Terashita, et al.(1993) are among the first researchers to apply the fractal analysis concept to evaluate the dispersion state. Their detailed observations of the large number of minute samples 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 3.12.
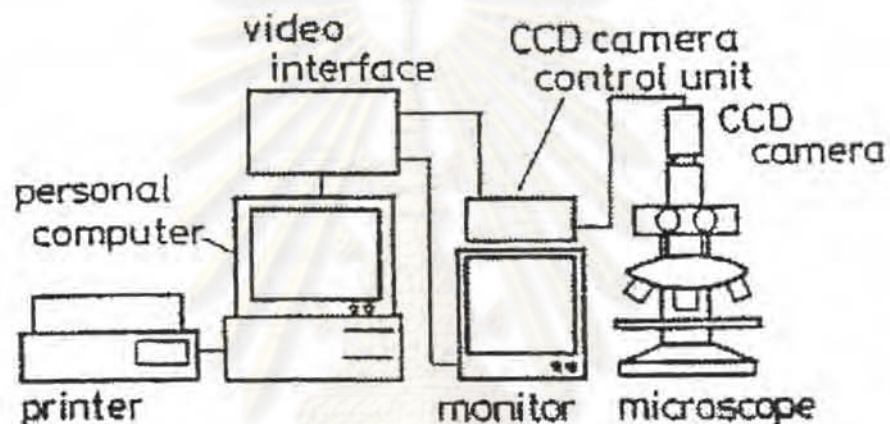

Figure 3.12 Schematic diagram of the image analyzer (Terashita, 1993)

Each sample 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. Based on this dealt image, the fractal dimension was to be determined as a quantitative representation of the dispersion state, as follows:

First, the dealt image was divided into n x n segments $(2 \leq n \leq 80)$ to yield n^2 segments. Next, for segment no. i, the area ratio S_{fi} of pigment particles was calculated as follows:

$$S_{fi} = A_{fi} / A_i \qquad (3.5)$$

where A_{fi} as the area occupied by the particles in segment no. i, and A_i was the total area of the same segment. A coefficient of variation Ds(n) was calculated from the mean value of S_{fi} for the applicable n (namely $\bar{S}_f(n)$) and the corresponding standard deviation $\sigma_s(n)$ as follows

$$Ds(n) = \sigma_s(n) / \bar{S}_f(n) \qquad (3.6)$$

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

$$Ds(n) \ \alpha \ (1/n)^{-D} \qquad (3.7)$$

then the particle dispersion state could be characterized by the fractal dimension (D).

Since linearity was observed over the range of $2 \leq n \leq 80$, as shown in Figure 3.13, the fractal dimension (D) could be calculated from the slope. Naturally, the fractal dimension D increased as the particle dispersion state improved.
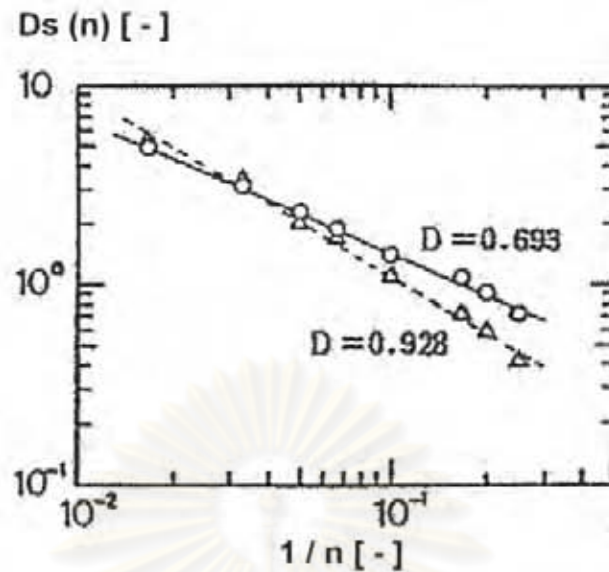
Figure 3.13 Example of calculation of fractal dimension (Terashita, 1993)

Figure 3.14 depicts two dealt images showing the filler dispersion state and its fractal dimension (D). In this figure, black spots and 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 particle dispersion state.
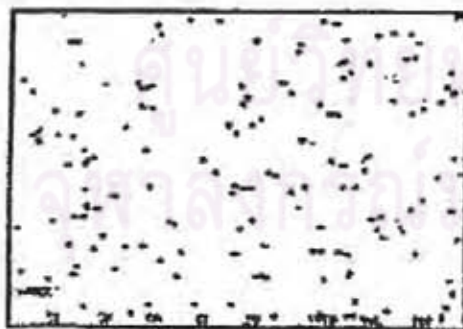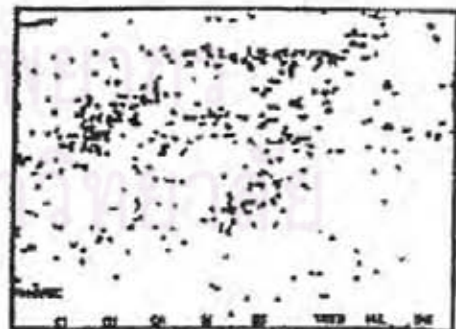
(a) D = 0.907   (b) D = 0.462

Figure 3.14 Dealt image showing filler dispersion state
and its fractal dimension (D) (Tarashita, 1993)

3) Fractal analysis in the present work

In the present work, although one of the pigment used was carbon black, the polymer used was polystyrene. So the despersibility should not be evaluated with ASTM D2663 which has been designed for carbon black dispersion in rubber. On the other hand, BS2782: Methods 823A and 823B are the methods of the assessment of dispersion of relatively large carbon black particles in polyethylene clearly visible with the aid of a microscope. Since the carbon black pigment size here is only about 0.095 μm, its evaluation could not directly apply these methods.

Here evaluation of the degree of dispersion of both pigments, iron oxide and carbon black, was carried out using the fractal analysis. As the median particle size of the pigments were very small; iron oxide 0.20 μm and carbon black 0.095 μm, and the wave-length of visible light (0.4~0.8 μm) was broader than the pigment size, ordinary micro-photograph was not applicable, Nor was light microscopy coupled with image analyzer which was employed by Terashita, et al.

To evaluate the fractal dimension based on the counting method, all prepared thin samples were dipped in liquid nitrogen and snapped in two. Then they were micro-photographed using scanning electron microscope (SEM). Each micro-photograph was divided in nXn subsections (n = 2, 4, 5, 8, 10, 16, 20, 40 and 80). At each similarity ratio (r), the number of subsections, $N(r)$, containing at least one or more pigment particles was counted. The relation between $N(r)$ versus r was plotted on the log-log scale to find the fractal dimension from the slope of the straight line, which was.

3.8 Ideal-case simulation of particle dispersibility in plastic

Computer experiments using Monte-Carlo technique can be used to simulate the ideal dispersion of pigment particles in a sample (Pijarn, 1994). In the present study, two ideal types of random patterns were used, namely, uniform random and normal random dispersion.

3.8.1 Uniform random dispersion

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

$$X = RNDX * XL \tag{3.8}$$

and
$$Y = RNDY * YL \tag{3.9}$$

where

X = the position of pigment particle on the X axis

Y = the position of pigment particle on the Y axis

RNDX, RNDY = uniform random number between zero and unity

XL = length of sample piece on the X axis

YL = length of sample piece on the Y axis

3.8.2 Normal random dispersion

In the ideal case of Guassian or normal random dispersion, the pigment particles were randomly but not uniformly dispersed around the center (X_o, Y_o) of a sample. The mathematic formulas used to simulate the position (X, Y) of a pigment particle on the sample (a unit square) are as follows:

$$X = Xo + RNGX / 3.0 \qquad (3.10)$$
and
$$Y = Yo + RNGY / 3.0 \qquad (3.11)$$

where

RNGX, RNGY = standard normal random number

(zero mean, unit variance)

X = the position of pigment particle on the X axis

Y = the position of pigment particle on the Y axis

Xo = 0.5

Yo = 0.5

The probability of RNGX or RNGY falling outside of (-3.0, 3.0) is very 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 were carried out on the properties, the present study decided to use the generators extensively tested by W. Tanthapanichakoon (1978).