CHAPTER 2

FUNDAMENTALS AND RELATED WORKS

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

2.1 POLYETHYLENE

Polyethylene (PE) is a major member of polyolefins. It is one of the most widely used polymers of the thermoplastic group. The basic structure of polyethylene is the chain, $-(CH_2=CH_2)_n-$. It is manufactured from ethylene by polymerization.

The two main types of polyethylene are low-density polyethylene (LDPE) and high-density polyethylene (HDPE) (Chanda, and Roy, 1986).

Low-density polyethylene is manufactured by free-radical polymerization at high pressures (15,000-50,000 psi) and elevated temperatures (200-35 0°C) in the presence of oxygen (0.03-0.1 %). It is an amorphous and branched product and had a melting temperature range of 107-120°C.

High-density polyethylene is produced in a low-pressure process using either Ziegler-Natta catalysts or metal-oxide catalysts (usually referred to as Philips catalysts). HDPE is essentially linear, having much less branching than LDPE, and has a melting range of 130-138°C.

Recently, low-pressure processes for the production of *linear-low density polyethylene* (LLDPE) have been announced. The LLDPE polymers are linear but

had a significant number of branches. The linearity provided strength, while the branching provided toughness.(Ulrich, 1982)

Polyethylene is partially crystalline and partially amorphous. Linearity of polymer chains affords more efficient packing of molecules and hence a higher degree of crystallinity. On the other hand, side-chain branching reduces the degree of crystallinity. Increasing crystallinity increases density, stiffness, hardness, tensile strength, heat and chemical resistance, creep resistance, barrier properties and opacity, but it reduces stress-crack resistance, permeability and impact strength. Table 2.1 shows a comparison of the three types of polyethylene.

Table 2.1 Types of Polyethylene (Chanda, and Roy, 1986)

	Chain Structure	Crystallinity	Process	Density (g/cm^3)
LDPE	Linear/branched	~ 50%	High pressure	0.912 - 0.94
LLDPE	Linear/less branched	> 50%	Low pressure	0.92 - 0.94
HDPE	Linear	< 90%	Low pressure	> 0.958

Polyethylene has excellent chemical resistance and is not attacked by acids, bases or salts. The other characteristics of polyethylene which have led to its widespread use are low cost, easy processability, excellent electrical insulation properties, toughness and flexibility even at low temperatures, reasonable clarity of thin films, freedom from odor and toxicity and sufficiently low water vapor permeability for many packaging, building, agricultural applications.

Major markets for LDPE are in food packaging products, industrial sheeting and trash bags, whereas HDPE is used mainly in blow-molding applications (milk bottles, household chemical bottles, fuel tank applications), in corrugated pipe, and in wire and cable applications.

2.2 COLORANTS

Colorant is a general term for describing the material used to impart color to objects. The two basic types of colorants used in plastics are pigments and dyes. It is not always easy to distinguish between a dye and a pigment. Generally, dyes are soluble under the conditions of use but must be completely dissolved, leaving no color streaks and little or no haze. Pigments are insoluble and consist of particles that must be dispersed by physical means.

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 2.1).
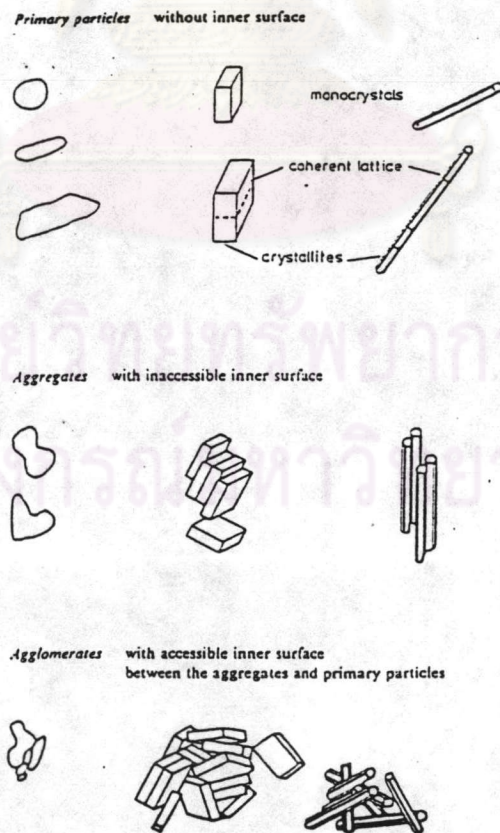

Figure 2.1 Elements of a pigment

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. 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.

Inorganic pigments (Mathew, and Campbell, 1989) are insoluble in both the solvents used in plastics and in the plastics themselves. In general, the inorganic colorants produce opaque dull colors, although some are translucent at low concentrations and some synthetic inorganic pigments produce bright colors at high concentrations. Compared to organic pigments, they generally have larger particle sizes and smaller surface areas and have a higher density and lower oil absorption, and provide better weathering.

Organic pigments are characterized by good brightness, color purity, and nearly transparent optical properties. They provide more color per unit fraction but are subject to migration, are less heat resistant, and are generally less light stable than inorganic pigments. Table 2.2 shows the popular organic and inorganic pigments for plastics

Dyes generally have higher optical transparency or clarity than inorganic pigments and many organic pigments. The major limitation of the use of dyes in polymers is migration or bleeding from several polymer types such as flexible polyvinyl chloride (PVC) because of the incompatibility of dyes in the system.

Table 2.2 Popular organic and inorganic pigments for plastics (Zeller, 1989)

Color	Inorganic	Organic
Reds (including maroon and violet)	Cadmium mercury	Carbazole violet
	Cadmium sulfoselenide	Disazo condensation
	Manganese violet	Isoindolinone
		Permanent Red 2 B
		Perylene
		Quinacridones
Blue	Cobalt aluminate	Phthalocyanine
	Cobalt blue	
	Iron blue	
	Ultramarine blue	
Yellow	Cadmium sulfide	Diarylide
	Chrome yellow	Disazo condensation
	Nickel titanate	FD&C Yellow #5
		Vat anthraquinone
		Monoazo (Hansa)
		Isoindolinone
		Nickel-azo
Green	Chrome green	Phthalocyanine
	Chrome oxide	
	Hydrated chrome oxide	
Orange	Cadmium mercury	Aniline
	Cadmium sulfoselenide	Disazo condensation
	Chrome orange	Monoazo (Hensa)
	Molybdate orange	Isoindolinone
Brown/Buff	Iron oxide	
Black		Carbon black
White	Titanium dioxide	

Source : Plastics compounding 1984/85 Redbook

2.3 COMPOUNDING

Adding and mixing colorants into plastic resins is an integral part of a much broader operation called compounding. Few resins are useful in their natural form; they are, therefore, mixed with other materials to improve or enhance their properties, making them more useful for a variety of applications. The process by which ingredients including the colorants and resins are intimately mixed together into as nearly a homogeneous mass as possible is known as *compounding*.

The importance of compounding to the plastics industry could not be overstated. A particular goal could be reached by employing various polymers, additives, compounding processes, and a variety of routes. The compounding line might be arranged in several ways; it involved many operations, each of which could be executed on more than one specific piece of equipment(Moloney, 1986).

Additives are substances incorporated in very small quantities to impart desirable properties into materials and to reduce adverse properties. There are many types of additives in plastics as shown in Table 2.2.

Table 2.3 Type of additives in plastics

Type of additives	Example
Processing additives	- Processing stabilizers
	- Lubricants
	- Processing aids
	- Blowing agents
Modifiers of mechanical properties	- Plasticizers
	- Reinforcing agents
	- Toughening agents

Table 2.3 Type of additives in plastics (continued)

Type of additives	Example
Modifiers of surface properties	- Antistatic agents - Slipping agents - Antiblocking agent - Adhesion promoters - Antiwear agents
Modifiers of optical properties	- Pigments and dyes - Optical brighteners
Performance extenders	- Antioxidants - UV-stabilizer - Thermal stabilizer - Metal deactivators - Fungicides - Antibacterial agent - Flame retardants
Cost modifiers	- Fillers -Diluents and extenders

In short, 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. Three groups of the plastics compounding equipment are:

Nonintensive Mixers (Maloney, 1986) 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. The following are examples of nonintensive mixers.
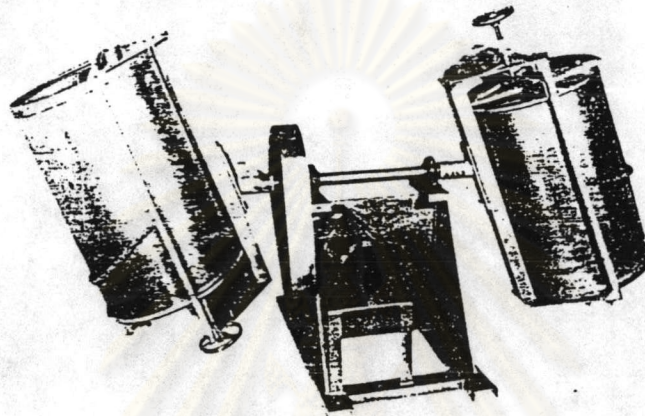

Figure 2.2 Drum tumbler (Maloney, 1986)

Drum tumblers use detachable drums that are partially filled with the ingredients, loaded onto a drive system, and set in motion. The simplest consists of two rotating shafts upon which the drum is laid horizontally (see Figure 2.2). Drum tumblers are limited by the sizes of the drums that could be conveniently loaded.
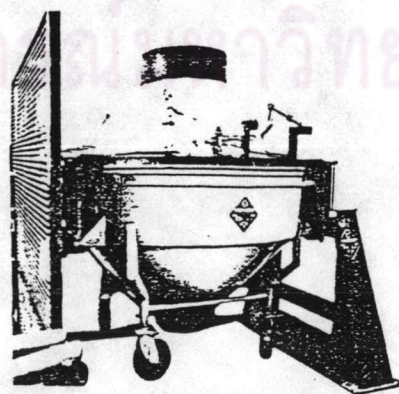

Figure 2.3 Double-cone blender (Maloney, 1986)

Double-cone blenders consist of two conical shells joined together by a cylindrical shell and attached to a drive shaft across a cylinder diameter. A typical double-cone blender is shown in Figure 2.3. As the double cone rotated, material is tumbled in the radial and tangential directions, and axial flow is provided by the impingement with, and sliding on, the conical section walls.
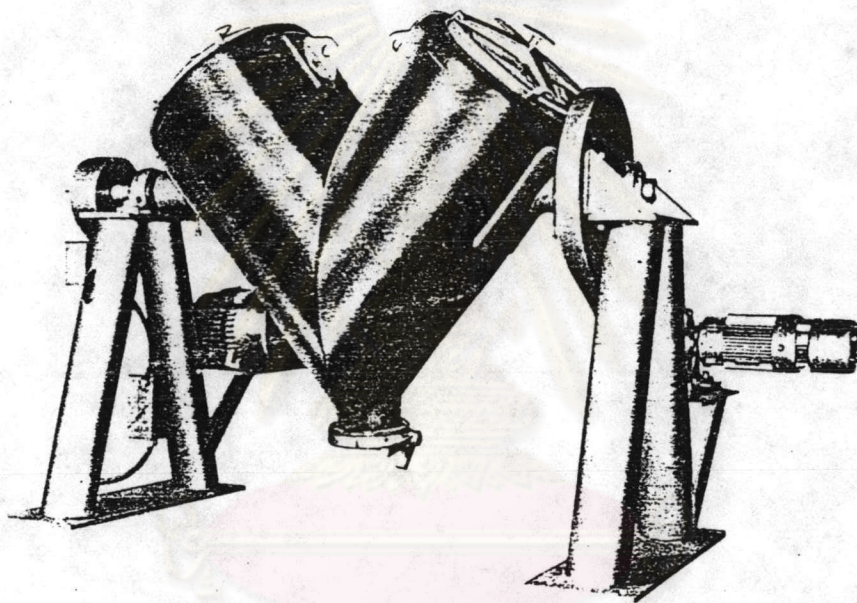
Figure 2.4 V-blender (Maloney, 1986)

V-blenders might also be used for tumble blending. In the general configuration shown in Figure 2.4, two cylindrical shells are joined perpendicularly and closed on the remaining ends. A shaft is then assembled to the V at 45° to both cylinders. The shaft-V assembly is partially filled with the necessary ingredients and rotated. The V geometry ensures mixing in all directions. Agitator shafts geared independently from the drive shaft might be mounted inside the V to provide more intensive or speedier mixing.
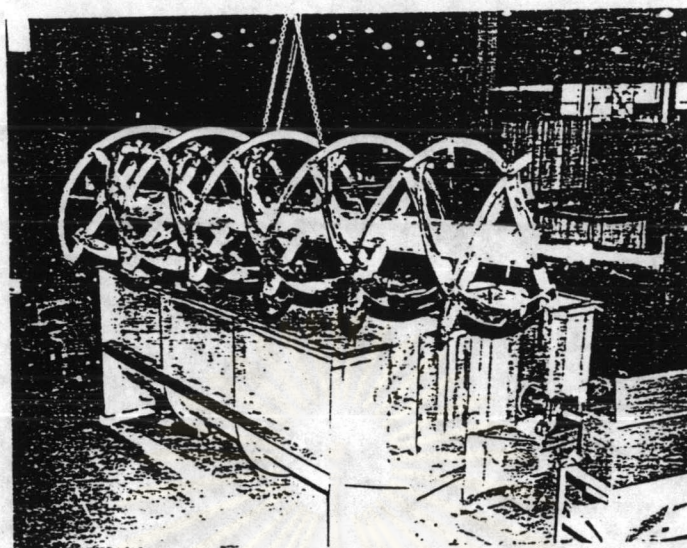
Figure 2.5 Ribbon blender (Maloney, 1986)

Ribbon blenders, probably the most common of batch mixers, are much larger than tumblers. A ribbon blender consists of a large cylindrical shell in which two spiral ribbons are mounted on a drive shaft (see Figure 2.5). The rotation of the ribbon in the cylinder provided mixing in all directions. For any unit, a number of ribbon designs are available to give a wide range of application. Unlike tumbling mixers, the units operate nearly full. Some units consist of two cylinders and ribbons mounted side by side; the walls between the ribbons are removed to allow cross-flow. Similar mixers are set vertically with a screw mounted in a conical shell.

Medium-intensity Mixers (Maloney, 1986) Mixing shafts are used in a wide variety of units known by the name of the inventor or the manufacturer. Such mixers included the Forsberg, the Marion, the Littleford, The Day, and the Willow Tech (see Figure 2.6). Their essential features are twin shafts with overlapping mixing plows. With this type of mixer, pastes and bulk molding compounds might be prepared, and ingredients fluxed. The mixing action is more intensive than in the mixers already described above. Another similar mixer is the sigma-blade mixer.

Its shafts or blades are designed to produce an intensive mixing action which, in most instances, fluxes the ingredients. Many other blade designs are available, permitting a wide spectrum of mixing actions which might be tailored to match the compounding requirements. Double-planetary mixers are less intensive. They are used to blend pastes, but can not flux solids, and are widely employed in preparation of plastisol, i.e. mixture of plastic and plasticizer. These mixers consist of drive shafts with intermeshing stirrers attached. Each revolves on its own axis and simultaneously orbits the mixing chamber. All the mixers described in this group are batch mixers.
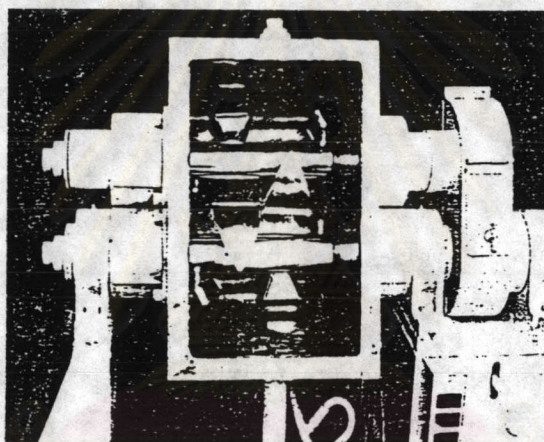

Figure 2.6 Willow Tech mixer (Maloney, 1986)

Intensive-fluxing Mixers (Maloney, 1986) The mixers in this group might be batch or continuous. Although the latter is preferred from an operational standpoint, some batch mixers are still used. The most well-known is the Banbury mixer, which had its origins 60 years ago in rubber compounding; today, it is widely used for polyolefins. The Banbury mixer consists of two spiral shafts which rotate about fixed centers in a counterrotating mode (see Figure 2.7). The spiral lobe on the shaft provides a degree of axial mixing which, coupled with the radial mixing across the gap and the tangential mixing between the rotor and the chamber wall, ensures excellent distributive mixing. Dispersive mixing occurs mainly in the clearance adjacent to the chamber wall. The Banbury is top-fed, and the ingredients

to be compounded might, of course, be added in stages. The motions of the spiral-lobed shafts ensure adequate melting. In fact, the chamber is drilled for circulation of a heat-transfer medium to remove excess heat. The time of mixing and pressure exerted by the ram might be varied to accommodate the material being compounded.
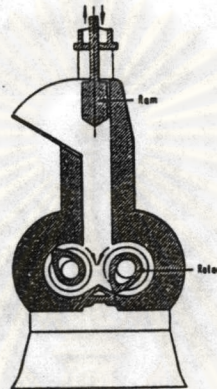
Figure 2.7 The Banbury mixer

The roll-mill batch mixer consists of two counterrotating rolls mounted on drive shafts (see Figure 2.8). Material bypasses the slightly faster-driven roll and is returned to the gap entry. At this point, it is distributed in the rolling bank and once more disperses as it passes through the gap between the rolls. The speed of the rolls and duration of mixing could be adjusted according to the requirements of the material.

Figure 2.8 The roll-mill batch mixer

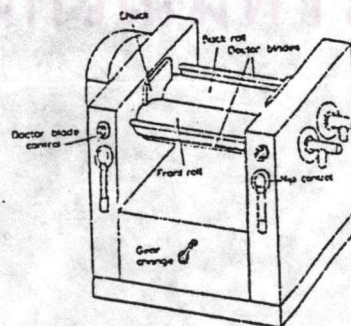Some compounding is performed on single-screw extruders which, however, frequently could not provide the required mixing intensity (see Figure 2.9). Since an intensive mixer is more expensive to purchase and operate, a single-screw extruder is preferred for compounding wherever possible. Its key element is a helical screw turning inside a stationary shaft and pushing the material toward the die. The barrel is heated, and the material, fed as solid particulates, melts. The melt is mixed by circulating in the channel. The additives are encapsulated by the melt and distributed by its circulatory motions. The melt is then pumped from the extruder as compounded polymer.

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.
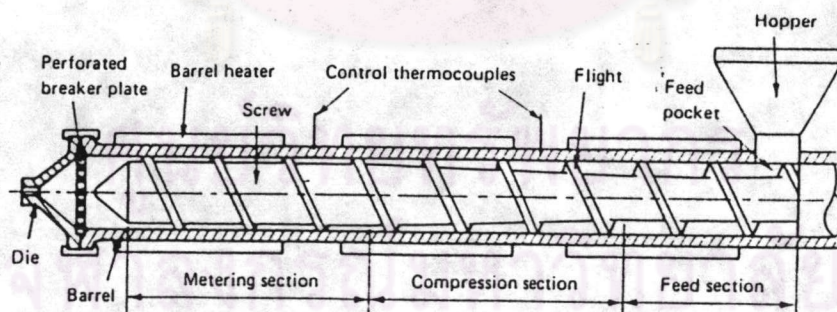

Figure 2.9 Single-screw extruder

Dual-diameter extruders accommodate feedstock with low bulk density. The large-diameter inlet and smaller-diameter outlet give high compression ratio.

The Transfer mix is an extension of the single screw extruder. In addition to the helical channels cut in the screw, reverse helical channels are cut in the barrel in the regions where the polymer is molten (see Figure 2.10a). As the screw rotates in the stationary barrel, the molten polymer is transferred back and forth between the screw channel and the barrel channel. This is achieved by appropriately varying the respective channel depths. Recirculating vortices in these channels ensure adequate distributive mixing, and the high shear plane between the channels provides some dispersive mixing (see Figure 2.10b). With a shallow screw channel, the recirculating polymer is only a fraction of that which might be forwarded. Therefore if, for example, a small amount of color concentrate is compounded with the polymer and collected in this shallow channel, where it constitutes a significant part of the material, it would be easier to mix. It is diluted as it is transferred to the deeper channel. This arrangement contributes to powerful compounding of color concentration, masterbatching, and direct dispersion of low percentage pigment or additive.
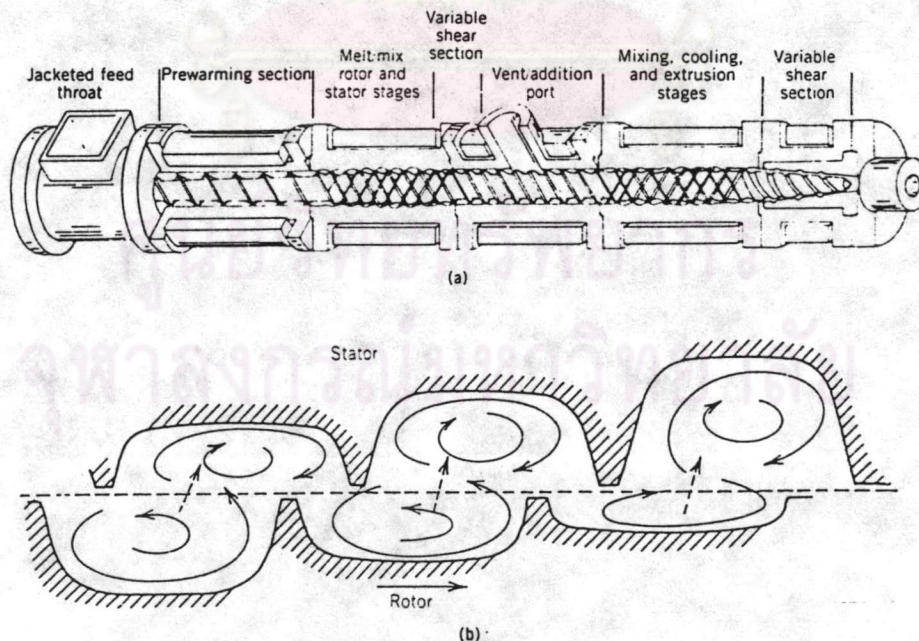

Figure 2.10 Sterlex Transfer mix (Maloney, 1986)

(a) double concentric screw extruder   (b) flow pattern for mixing per stage

Kneaders are single-screw extruders which provide the rotation of the screw in the barrel and a reciprocating axial movement. Unlike other single-screw units, the flight on the kneader screw is interrupted, usually three times per lead. These flight segments provide one-half of the kneading gap. The other is provided by inserting pins that protrude from the wall of the barrel (see Figure 2.11). As the screw turns and reciprocates, the pins form narrow gaps with the flight segments in such a way that all sides of the flight segments and pins are wiped, material hang-up is thus avoided.
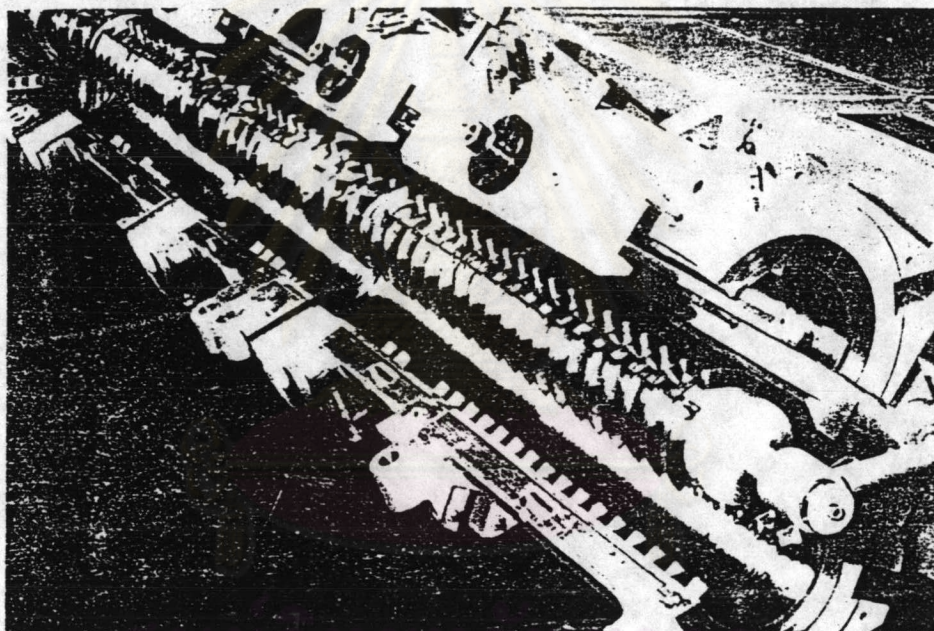
Figure 2.11 Buss-Kneader (Maloney, 1986)

The two commercially available kneaders are the Buss-Kneader and the Baker Perkins Ko-Kneader. The Buss-Kneader has segmented screw and barrels, and the pitch might be varied along the length of the screw without replacing the screw. Both types have a clamshell barrel for easy maintenance and cleaning. Both units have provision for cylindrical pins or pins with a parallelogram cross section to achieve the appropriate shear stress in the gap for a certain time. In addition, the

Buss-Kneader could be fitted with restriction rings which provided dams across the channel and throttle the forward conveyance of material, imparting extra mixing.

Neither the Buss-Kneader nor the Ko-Kneader could generate high pressures. Except for dies with low restriction, the unit must be coupled with a single screw crosshead or in-line extruder to provide the pressure necessary to force the material through the die.

Twin-screw extruders, in contrast to single-screw units, have two screws mounted in the parallel in a single barrel with a figure-eight cross section (see Figure 2.12). In corotating units, the screws rotate in the same direction. These highly successful units are now available from many manufacturers. For flexibility, corotating twin-screw extruders are constructed with screws and segmented barrels, allowing a wide choice of L/D ratio (length to diameter ratio). Therefore, segments might also be arranged, if necessary. For example, melt addition of an antistatic agent in the sixth-barrel segment without supplemental hardware.
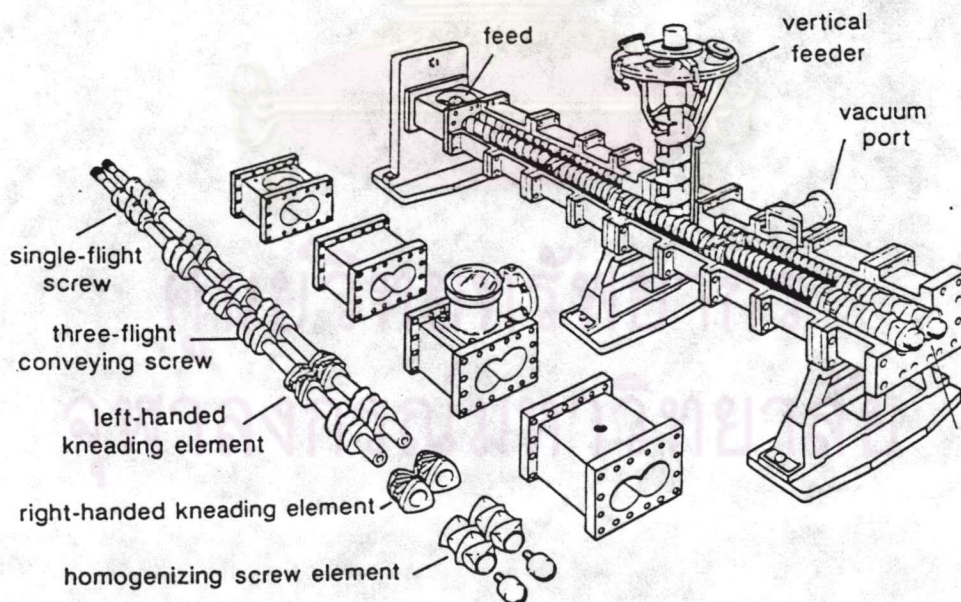
Figure 2.12 Twin-screw extruder

The screws for corotating twin-screw extruders could vary in several ways. The number of channels could vary from one to three. The more channels, the

more intensive the mixing. Some units use the same barrel for screws with different channel numbers and even allow the channel number to vary along the length of the shaft. The screw elements are available in a variety of shapes, e.g., deep channels for the conveying of solids and devolatilization, shallow channels for melting and melt conveying, kneading blocks for dispersive mixing, reverse flights, reverse kneading blocks and neutral kneading blocks for restricting forward conveyance. Screw design is made by trial and error until a satisfactory product is obtained. In another variation, dual diameters aid in compounding highly filled materials.

The counterrotating twin-screw extruder is a versatile intensive mixer similar to the corotating twin-screw extruder except that the screws are driven in opposite directions. This changes the geometry of the screws considerably and allows the unit to have a completely positive-displacement pumping action. Because the bulk density of the solids feed is vastly different from that of the melt, some units are made with conical screws to allow a compression ratio. Compression might also be achieved by varying the channel depth. The channels might be cut in such a way that the channels are lengthwise or crosswise open or closed. Segmented screws are also available with elements similar to the corotating units. One manufacturer provides a nonintermeshing arrangement where the intensity of mixing is between that of single-screw extruders and intermeshing twin-screw machines.

Multistage machines offer the advantages of both the twin-screw corotating extruders and single-screw extruders (see Figure 2.13). They consist of two stages with a twin-screw corotating unit or a unit for conveying and melting the ingredients. A single screw pumps the mixture to a die. The two extruders might be arranged perpendicularly on a horizontal plane or perpendicularly with the first stage mounted vertically. A great variety of screw elements is available for the twin-screw stage, the barrel is of the clamshell type. Valves inserted in the barrel control the forward flow of polymer, which affords control over mixing intensity

and enables the unit to compound a wide variety of polymers with the same screw configuration. The single-screw stage ensures excellent pressure generation. Devolatilization is easy, since the vent is in a region polymers should never reach. However, two-stage units take up more floor space than single-stage units. For some unusual application, three-stage machines might be used.
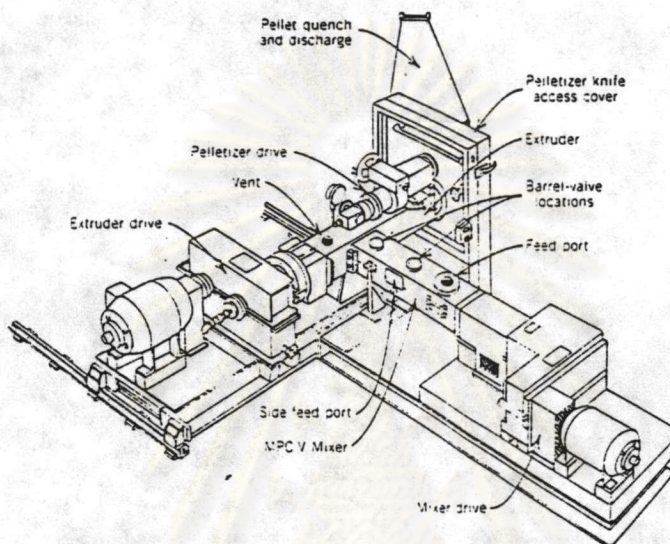
Figure 2.13 Multistage machine (Maloney, 1986)

The planetary-gear extruder consists of a single-screw extruder to which a planetary-gear unit is attached. The sun wheel is connected directly to the rotating extruder screw, and the annulus to the barrel. A number of planet gears are placed between the annulus and the sun wheel. The planetary-gear section could be considered as a mixing section on a single-screw extruder. It provides a highly intensive action which leads to dispersive mixing sections. The feeder screw moves solid material to the planetary-gear section, where it is plasticated and mixed. These units are commonly used for processing PVC powders, but are by no means restricted to these materials. The PVC application is able, owing to the ability of the planetary-gear extruder, to operate at high output without excessive heat generation because the material is spread out in thin layers, i.e., 2 mm, between the gears and is not insulated from external cooling sources. Furthermore, the high

shear is not continuous. To ensure that residence time in this region is not too long, all gears have a 45° helix angle that pumped the material toward the exit die. Provision might be made in all intensive-fluxing mixers to devolatilize the melt with a vacuum-venting arrangement.

2.4 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. As 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.

2.5 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.

2.6   EVALUATION OF DISPERSIBILITY AND QUALITY OF DISPERSION

If pigments are to be used efficiently, more information about their behavior in a dispersing environment is required. Several attempts have already been made to devise methods of measuring the quality of dispersion and the way it changes with mixing. Most of this effort has centered on the "tinting strength" test, although a method based upon particle size analysis has recently been developed.

The tinting strength of phthalocyanine blue in a white paint base has been shown to be directly related to its particle size. This provides a technique which might be applied to a plastic medium, in which a standard white base is mixed with the pigment being examined. The resulting depth of shade, or tinting strength, is proportional to the level of dispersion of the colored pigment. A comparison is usually made between the sample in question and one or more controls, which is made under conditions especially chosen to give high or low dispersion. For an exact comparison of shades, spectrographic curves should be used, but direct colorimetric measurements are usually sufficiently precise to be used on most occasions.

There are, however, a number of associated problems. The level of dispersion can have a pronounced effect upon the shade of the final color and upon the transparency of a colored pigment. Since the same amount of white pigment is always used so that the total amount of scattering should remain almost constant, it is assumed that this pigment remains unaltered during subsequent processing. Finally, large color-pigment particles appear as nearly black specks in the mixture and therefore make only a small contribution to the color.

There are other methods by which the size characteristics of pigment particles might be examined, although most are rendered useless by the presence of the solid polymer matrix which surrounds the particles in plastics. Of course, a

microscope could be used, as it has been in the past, despite the inherent tedium and subjectivity normally associated with its use. The recent appearance of automatic particle counters has largely removed these objections and has assisted in the development of procedures which counted and size particles at high speed. There are several particle counters currently available, but only the *Quantimet* has achieved wide acceptance.

The measurement of the degree of pigment dispersion is a difficult task. Only the large particles can be observed under an optical microscope. One convenient and accurate measuring method is to prepare a 5-mil pressout of the colored plastic. A small portion of this can then be mounted for viewing in a regular optical microscope at 400X. Use of a graduated scale superimposed on the field facilitates estimation of aggregate size. Direct observation of films or press-out plaques also serves as a qualitative guide. Grossly poor dispersions appear to be hazy and even to have visible color particles present.

A qualitative estimate of the degree of dispersion can also be obtained indirectly by measuring those properties of the colored plastics which are dependent on the presence or absence of large particles of pigments. Some of these properties are: flow of melt through extremely small apertures, electric faults in a wire coating, clogging time of a filter, and the physical strength and integrity of fibers and thin films.

2.7 LITERATURE SURVEY

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 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, is investigated. It was clear 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 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 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 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 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 was, as 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) studied about analysis of dispersion quality in highly pigmented polymer systems using scanning electron microscopy and image analysis techniques. This 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 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.

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 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 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 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 with 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 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 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 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 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.

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 metalized 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 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 coordination number. According to the evaluation, the fillers were dispersed in a uniform state if the value of 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.