Chapter II

Literature Survey

2.1 Principles of Pigment Dispersion in Plastics [15]

2.1.1 Initial Wetting

Initial wetting requires that the pigment and vehicle be sufficiently well-mixed and have sufficient affinity for each other to avoid separation when further work is applied to the system. In dry-blending, the tendency for pigment to pelletize or cake on equipment and the amount of loose pigment present following such a blend are measured of initial wetting. The importance of initial wetting is often underestimated because of the usually simple means by which it is obtained. Yet, it is not only essential, but often controls the quality of the final dispersion, or at least the amount of time required to obtain it. Surfactants can aid in increasing the affinity between pigment and vehicle, thereby improving the quality or reducing the time needed to obtain initial wetting.

However, pigments vary substantially in their chemical composition and surface characteristics, so no single surfactant should be expected to serve all situations equally well.

2.1.2 Size Reduction

Size reduction may be achieved by impact, particle-to-particle attrition, or by shear transmitted through an intermediate fluid layer. In any case, sufficient mechanical energy must be introduced to overcome forces holding aggregates and agglomerates together. Because this is often carried out in the presence of a vehicle, physical characteristics of the vehicle can be extremely important.

2.1.3 Intimate Wetting

Intimate wetting is the process of replacing the envelope of air surrounding each pigment particle. An obvious benefit of air displacement is reduced attraction between particles, which might otherwise produce flocculation in systems where flocculation can occur.

The fundamental need for some degree of intimate wetting, however, it can promote a strong bond between pigment and vehicle enough to withstand forces which applied to the system in later processing. Particularly, those intentionally introduced in melt or liquid shear dispersion processes to fracture agglomerates.

The theoretical discussion on dispersion mixing can be summarized as follows [12].

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 will occur.
4) Larger agglomerates will 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.

2.2 Dispersibility [16]

Dispersibility of a filler is established primarily by (1) the chemical nature of the filler, (2) its surface characteristics, (3) its particle size, and (4) the process by which it is made. The chemical nature of the filler defines the bond strengths and many of the special surface characteristics that will be encountered in any given material. The physical and chemical properties of the filler surface will establish its tendency to aggregate and the strength of the clusters formed.

Particle size of the filler is also important to its ease of dispersion. In general, the surface energies of particles greater than 1 μm are such that the driving force for aggregation is minimal and the aggregates that do form are generally weak. As the particle size drops below 1 μm, and particularly as it enters the colloidal region below 0.1 μm, the tendency of the particles to aggregate in large clusters increases progressively and substantially. In this region, protective colloids or surfactants must also be employed to stabilize the particles from reagglomerating once the initial aggregates are broken during the dispersion process.

Finally, the processes by which the fillers are produced have an all-important effect on the ultimate dispersibility of the product. Favorite techniques include (1) the use of various surface treatments to change the surface chemistry and reduce the forces of particle-particle attraction and bonding and (2) methods to circumvent the drying process or reduce the forces of agglomeration that occur during drying.

Proper dispersion is essential to the performance and ultimate success of the filled system. Figure 2.1 shows a poor dispersion, while Figure 2.2 shows a good dispersion of filler particles in matrix.
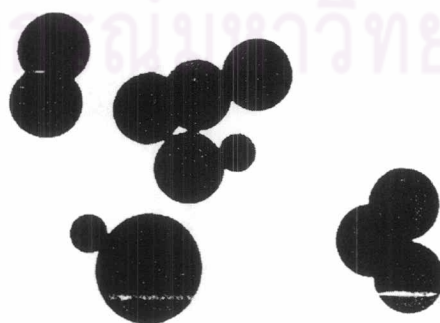
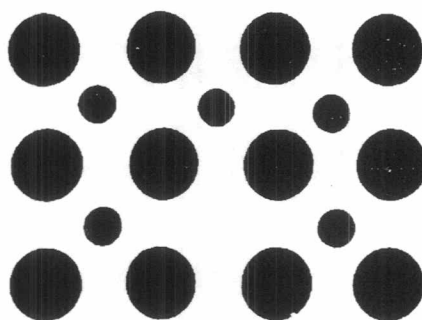Figure 2.1   Agglomerated filler in matrix

Figure 2.2   Filler dispersed to discrete size in matrix

2.3   Dispersion Methods [12, 16]

In compounding, three basic dispersion processes are commonly used : dry blending, melt shear, and liquid dispersion.   In practice, a combination of these techniques is often employed.   The experience of the compounder is still the primary factor determining the dispersion processes used.   The basic dispersion processes for pigment-plastic systems are summarized as following.

2.3.1   Dry Blend Dispersion

The dry-blending technique achieves dispersion primarily by impact and attrition grinding.   Unless followed by another dispersion process, there is little opportunity for effective wetting of the pigments by the resin.

2.3.2   Melt Shear Dispersion

Melt shear dispersion is most commonly employed in thermoplastics compounding and works well in follow-up combination with dry blending.   The effectiveness of melt shear depends on the ease of wetting of the filler by the polymer and a high enough viscosity to allow high shear forces to be effectively transmitted to the filler aggregates.

2.3.3   Liquid Dispersion

Liquid dispersion processes for plastisols involve predispersion of the filler in the plasticizer.   Equipment type can vary, but the type of dispersion forces is generally determined by viscosity, which is most often controlled by the filler concentration.

In practice, a combination of these processes is often employed to take advantage of the merits of each. For example, intensive dry blending before melt dispersing can 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. The choice of dispersion technique usually is dictated by cost, the ultimate property requirements of the filled composite, and, finally, the dispersibility of the fillers required to provide those properties.

Since this work has been focused on the study of dispersibility of organic pigments in MDPE via dry and melt blending techniques on their mechanical, physical, and thermal properties. Therefore, some researches related to this work are reported as follows [9].

Dobbin, C.J.B. and Baker, W.E. (1992) studied the analysis of dispersion quality in highly pigmented polymer systems using scanning electron microscopy and image analysis techniques. The paper showed the use of scanning electron microscopy (SEM) in conjunction with a commercial image analysis system to quantitatively characterize particle dispersion in polyethylene color concentrates. Compounds containing high loadings of organic and inorganic pigments were evaluated directly in order to avoid agglomerate reduction resulting from sample dilution. The effects of various processing conditions and additives on dispersion quality were also examined. The results showed that in the area of polymer color concentrates, the method and conditions of preparation had a fundamental effect on dispersion quality. In their study, two highly pigmented polyethylene systems were examined using scanning electron microscopy with the resulting images characterized using computer-driven image analysis techniques. Agglomerate levels were determined numerically and correlated to process conditions. The effect of certain additives on pigment dispersion was also explored.

Teshima, T., Yabe, N., Terashita, K., and Miyanami, K. (1993) investigate the effect of mixing time on dispersion of the toner compositions. These were composed of

thermoplastic resin, carbon black, and a charge control agent which is a material for toner. These compositions were mixed with a stir type mixer at various mixing times. The mixing process was investigated by measuring the load ratio and temperature of the mixture during the mixing operation, and the state of the mixture were examined by SEM observation, X-ray microanalysis. 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.

In-eure, P. (1994) studied the effects of kneading conditions on the dispersion of pigments in polyethylene using a continuous kneader. The kneading temperature, the rolling temperature, the speed of rotation (twin screw), and the particle size of pigment particles were studied. This study used a fractal analysis method to evaluate the dispersibility of pigment in polyethylene. The results showed that the higher the kneading temperature, the higher the dispersibility of pigment in polyethylene, but at the higher kneading temperature the process becomes more of mixing than dispersion. The dispersibility of the pigment increased as the rotational speed of the screw increased since a higher speed provided higher intensity of shear stress to break agglomerates of the pigment, so that the pigment could disperse better than the smaller one. Finally, the rolling temperature had no significant effect on the dispersibility of the pigment. It only affected the internal structure between the pigment and polyethylene.

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

Phingchin, N. (1996) investigated factors influencing the dispersion of pigments in polystyrene upon using a continuous twin-screw kneader to find the most suitable kneading conditions. This study also applied a fractal analysis method to evaluate the

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

Thongchiew, A. (1996) reported factors influencing the dispersion of organic pigments in polyethylene upon using a continuous twin-screw kneader. The studied parameters were the kneading temperature, the rotational speed of twin-screw, the feed rate and the premix time in order to determine the suitable kneading condition. The fractal concept was applied to evaluate the dispersion state of pigments. Raw materials used in the study were two organic pigments, carbon black and quinacridone violet pigment, and high density polyethylene resin (HDPE). In addition, effects of the kneading conditions on the tensile properties of HDPE kneaded with either pigment were also investigated. It was found that the dispersibility of either pigment increased as the kneading temperature and the rotational speed increased, and that the higher the feed rate was, the lower the dispersion state of the pigment became. The premix time, upwards of 10 minutes of primary mixing, had insignificant influence on the kneading result. As for the effect of the kneading temperature on the tensile properties of polyethylene with pigment, it was found that as the kneading temperature and the rotational speed of screw increased, the kneaded HDPE turned harder and more brittle, especially at kneading temperatures above 220 $^{\circ}$c. Incidentally, comparison between the carbon black and quinacridone violet pigments revealed that the carbon black pigment, which had a smaller size (approximately one-sixth of that of quinacridone violet) and less polarity, provided more uniform dispersion state and better properties of the polymer blend.

Horiuchi, S., Kajita, T., and Tachibana, T. (1999) [17] examined the dispersion of the pigment in LDPE by dry – impact blending method. Dry-impact blending method

was employed to prepare hybrid particles composed of fine particles of phthalocyanine blue and a coarse particle of low-density polyethylene (LDPE). A simple mixing in a Henschel-type batch mixer of the two kinds of particles, which were largely different in the size, at ambient temperature applying high stress produced hybrid particles, where the fine particles are distributed on the surface of the core particle. The surface appearances and the cross-sectional views of the particles were observed by scanning and transmission electron microscopy. It was revealed that the hybrid particles exhibited a capsule formation with the LDPE core coated with the phthalocyanine layer, where the phthalocyanine fine particles were embedded in the LDPE core particles. Consequently, the hybrid particles which were prepared, helps fine dispersion of the pigment into the LDPE matrix, and the pigmented LDPE sheet shows excellent color quality.

2.4 Forces Involved in Pigment Dispersion [18]

There are two principal types of force acting in the pigment dispersion process to bring about mechanical disruption of particle clusters : crushing and shearing. These are illustrated diagramatically in Figure 2.3. In most industrial dispersion equipment (commonly referred to as mills), both types of force will operate to a certain extent although depending on the action of the particular mill, either one or the other may dominate. Crushing involves impact forces, often due to projectiles (e.g., balls or beads), moving at high speed and giving rise to disintegration of pigment agglomerates. These forces are of particular importance in milling equipment such as ballmills, sandmills and beadmills. These mills are commonly used for dispersion of pigments into relatively low viscosity media such as paints and liquid inks, where sufficiently high impact velocities may be achieved. In contrast, shearing forces result from stresses exerted within a high viscosity fluid as the fluid flows, and these in turn cause mechanical breakdown of the pigment agglomerates. For efficient shearing, the flow pattern within the fluid must be laminar, a type of flow which is characterised by a regular linear flow pattern. The chaotic movement of fluid which is caused by turbulent flow conditions gives efficient mixing of the ingredients in the formulation but a poor dispersion results due to the low shearing forces which are generated under these

conditions. Shearing is the principal force involved in dispersion of pigments into high viscosity media such as paste printing inks, for example those used for lithographic printing, and into molten thermoplastics.
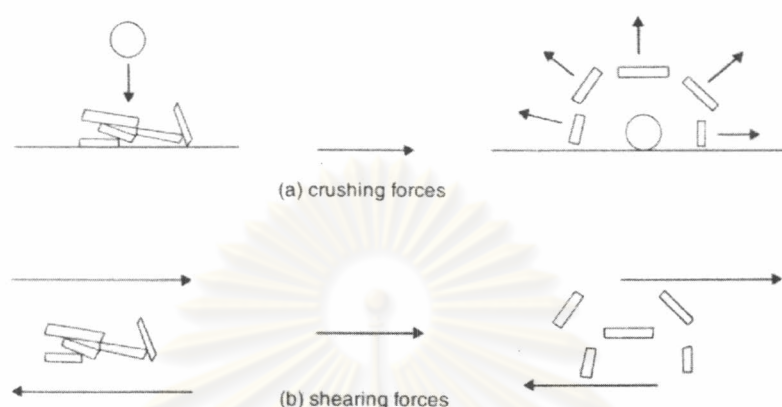

(a) crushing forces

(b) shearing forces

Figure 2.3   Mechanical disruption during pigment dispersion

2.5   Compounding [19]

Compounding is the process of mixing various additives with a base plastic material. Most plastics materials cannot be processed in their natural post-polymerized condition. Post-polymerized plastics are the raw materials, they must be enhanced for processing. Plastic materials without process additives decompose during processing and produce useless products. Early compounding technology focused on the addition of additives that enhanced and stabilized the material during manufacturing. Today the compounding of additives plays a large role in modifying the properties, imparting technical advantages, and enhancing the performance characteristics of plastic materials in all their product applications.

The development of new uses for plastics materials largely depends on the creative use of additives. There are thousands of additives; but each one fall into 16 different categories. Additives formulated to improve process ability are called process additives.   Process additives improve the materials ability to be melted, molded, shaped, and compressed without decomposition. If additives are used to provide stable products, these are called functional additive. Functional additives improve the plastic's product life by enhancing the chemical, physical, and environmental properties of the

material. In recent years the extensive use of plastic materials has been due to the development of functional additives. However, plastics materials can only be produced with the addition of both process and functional additives.

Compounding relies on the understanding of mixing principles. Mixing principles deal with the production of a homogeneous mass, uniform in composition and structure. There are three basic mixing principles that must be considered.

First, the surface area between the components must be spread so that more of the materials are in contact with each other. In compounding this is accomplished by melting the plastic and kneading, smearing, folding, stretching, wiping, compressing, and shearing it with the additives. In addition, the rate of shear and the mixing forces must be uniform throughout the compounding process. All portions of the plastic material must follow the same path, experience the same shear and heat history. Third, the additive must be distributed equally throughout the mixture to form a uniform mix. Compounding is accomplished by shearing the plastic's melt at right angles in the direction of flow, controlling the speed or shear rate, and by varying the gap between the stationary and rotating elements of the mixing device.

2.6 Colorant Forms and Methods for Incorporating Colorants into Plastics

Colorants can be introduced into plastics by several methods. A correct incorporation method speeds production, upgrades quality, and reduces cost. Thermoplastics are handled differently than thermosets in that the internal coloring of thermoplastic resins requires heating whereas the internal coloring of thermosets avoids heating [20, 21]. Conclusively, accepted colorant forms commonly used to pigmented plastics are listed in Table 2.1.

2.6.1 Dry Color (or Dry Colorant)

Dry coloring is one of the basic methods for incorporating colorants into thermoplastics. It offers the advantages of an almost unlimited color range (capable of matching nearly any specified color from a limited colorant inventory), little waste, and extreme flexibility in production (quick switch over to other colorants). On the other hand, the dry mixing may generate colorant dusting (with possible contamination of other plastics in the area) and the dispersion attained is less complete than that obtainable by precolored methods. Although dry coloring is relatively simple, certain

precautions must be observed. Colorants must be weighed with accuracy, the timing of the tumbling stage must be uniform from batch to batch (and preferably at a location apart from other processing operations), and the resin itself must be dry. Even if dry resins are used, it is normally necessary to dry moisture-sensitive resins after addition of the colorant and before molding. In addition, dry concentrates do not settle or separate and are cleaner to handle than paste. Dry color may be used in compounding when intensive mixers are used, but housekeeping and health considerations must be taken into account.

Table 2.1   Colorant forms commonly used (U) to color plastics [21]

Plastics	Colorant Forms			
	Dry Colorant	Dry Colorant Concentrate	Paste Colorant	Precolored Resin Masterbatch
Thermoplastics[a]				
Acetal	U	-	-	U
Acrylic	U	-	-	U
Cellulosic	U	U	-	U
Nylon	U	-	-	U
Polyethylene, Polypropylene, Polystyrene	U	U	-	U
Polycarbonate	U	-	-	U
Fluorcarbons	U	-	U	-
Thermosets				
Phenolics	U	-	-	U
Epoxies	U	-	U	U
Polyurethane	U	-	U	-
Polyester alkyd	U	-	U	-
Aminos	U	-	-	U
Diallyl phthalate	U	-	U	U

[a] Vinyls use all four forms

2.6.2 Precolored Compound (or Precolored Resin Masterbatch)

Extrusion coloring is concerned primarily with thermoplastics. Here use is made of precolored resin compounds (highly colored intermediates that provide better colorant dispersions and more uniform color). The colorant ingredients are first thoroughly mixed with resin in the dry blender and then charged to an heated extruder where the feed screw mixes the fused resin and colorant mixture. The continuous extruded colored strands (approximately 1/8 in. diameter) are either air or water cooled and then cut into pellets. Occasionally the strands are cut before cooling (say for polyolefin resin) in which case the pellets assume a more spherical shape.

Precolored compound finds decreasing use in industry. The rigid PVC industry, which up until the late 1970s used precolored compound extensively, now relies on in-house compounding or color concentrate.

2.6.3 Color Concentrates (or Dry Colorant Concentrate)

Color concentrates are concentrated mixtures of colorant in resin (the concentrate may contain ten times the proportion of colorant needed in the finished plastic item). The term commonly refers to a chip or pellet form of colorant for use in polyolefins and vinyls. However, liquid and paste color concentrates are use extensively to color vinyl compounds.

Special equipment is required to make a color concentrate since a high percentage of colorant is being added (10-15 %w colorant). Multiple passes through an extruder are effective but expensive. Two-roll rubber mills have been used very successfully but Banbury mixing has been found both satisfactory and economical for volume production. The use of color concentrates eliminates the housekeeping problems associated with dry color and assures the processor that the color has been developed to optimize its properties.

2.6.4 Pastes (or Paste Colorant)

Thermosetting resins supplied as powders (urea, melamine, phenolics) are commonly colored by mixing in a machine that blends the resin and colorant without too much generation of heat (ball mills and attrition grinders). Thermosetting resins

supplied as liquids (polyesters, epoxies) do not lend themselves to the addition of dry colorants because lumping, settling, and premature curing or hardening may take place. Rather, the method for coloring the thermoset resin depends on the method of fabrication. In the case of a molding operation the colorant is added in a liquid or paste concentrate form (a highly concentrated mixture of the colorant made by grinding the colorant into the liquid resin).

Thermosetting resins also use paste concentrates since the molder or fabricator easily achieves both complete dispersion and excellent color development with this form of colorant (used almost exclusively with liquid thermoset resins). Paste concentrates are also widely used with thermoplastic vinyl compounds. The paste dispersion may vary in consistency from a pourable syrup to a heavy paste. Paste concentrates are normally employed only when dry pigments are not satisfactory since the added grinding step necessary to make the paste renders them more expensive.

The tendency for pigments to agglomerate in a dispersion is a continuing problem. In the case of both organic or inorganic pigments this may be induced by the presence of an impurity or residual soluble salt. Since organic pigments are softer, they are more susceptible to this agglomeration tendency [21].

2.7 Pigments

The successful marketing of a plastic product is closely keyed to the "right" choice of an attractive and pleasing colorant to provide sales appeal and customer acceptance. The range of colored plastic products is extensive and growing, and includes such diverse items as packaging, automobile upholstery, canister sets, pens, telephone sets, and toys. Color in plastics is a desirable feature for marketability and identification. Although colors specified to fulfill these ends are based on esthetic principles, achieving the desired colors is based on physical, chemical, and engineering principles.

Colorants are defined as materials that will modify the light incident on a surface so that light of other wavelengths, at the same or lesser intensities, is reflected or transmitted [20]. Colorants are generally colored materials, although optical brighteners that reinforce color appearance may themselves be colorless. Colorants can be

incorporated into the plastic mass or applied to the surface of the plastic as a coating or laminate.

There are basically two types of colorants : those that are soluble in the formulation (dyes) and those that are insoluble (pigments). A comparison of the general characteristics of dyes and pigments is contained in Table 2.2. Some pigments show slight solubility, although such manifestation is generally undesirable and considered a defect. Solubility leads to bleeding or migration, plateout, and crocking, and might lack for the other properties, like pigment which has acceptable properties [20].

Table 2.2   A comparison of the general characteristics of dyes and pigments [18]

Characteristic	Dyes	Pigments
Solubility	Required to be soluble or capable of solubilisation especially in water	Required to resist dissolving in any solvents which they may contact
Traditional applications	Textiles, leather, paper	Paints, printing inks, plastics
Method of application	Applied to textile fibers from an aqueous dyebath solution	Dispersed into a liquid medium which subsequently solidifies
Main chemical types	Organic only : azo, carbonyl and arylcarbonium ion	Organic types : azo, phthalocyanine and carbonyl; inorganic types
Application classification	For textile applications, the subdivision into dye application classes is of considerable importance	Pigments are multi-purpose materials and application classification is relatively unimportant
Color properties	Full range of colored species	Include colored, white and metallic species

2.7.1   The Nature of Pigment Particles [18, 22]

Pigments are finely divided solid materials consisting of clusters of particles. Primary particles are the smallest pigment particles not normally further subdivided. However, during the manufacture of pigments, and especially at the stage where the pigments are dried to produce a powder, particles tend to cluster together. Two different types of particle clusters can be considered : aggregates and agglomerates. Aggregates are considered to be groups of primary particles joined at faces. Agglomerates are considered to be groups of aggregates or primary particles joined at edges and corners. These types of particles are illustrated in somewhat idealised form

in Figure 2.4. Because of the nature of the particle contact, agglomerates are much less tightly bound together than aggregates and are therefore easier to break down by dispersion.
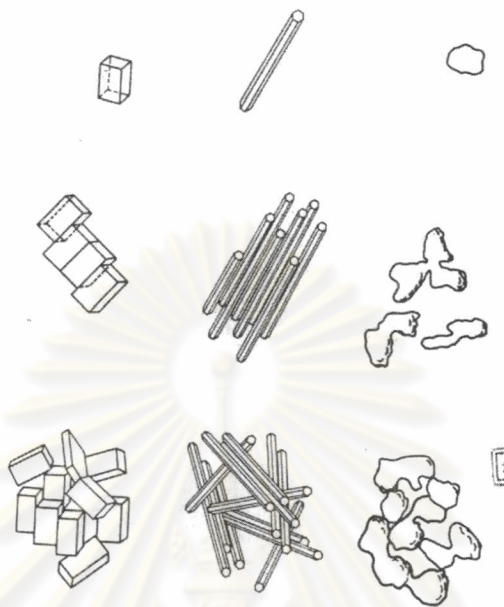

Figure 2.4   Types of pigment particles : primary particles, aggregates,
and agglomerates [22]

2.7.2   Selection of Pigment Colorant [20, 21]

The selection of a pigment colorant, aside from its hue, depends primarily on the nature of the plastic, the level of colorant, and the plastic end use.

1. Nature of Plastic

The plastic resin (and it processing method) are critical factors in the selection of a pigment for its coloration. If a plastic is processed at high temperatures, the pigment must accordingly be heat resistant.

2. Level of Colorant

The ratio of colorant to resin varies the color effect. In general, high concentrations of colorant are more lightfast than low concentrations (tints). However, in the case of certain red pigments, progressing to high concentrations promotes "bronzing." Low concentrations of colorant minimize "bleeding" and "crocking" tendencies.

Some pigments (iron oxides, phthalocyanines) have an antioxidant effect and when used at high levels can inhibit the cure of certain catalyzed plastic polymers.

3. End Use

The intended application of the plastic product is an important consideration in the choice of pigment colorant. If the plastic is in contact with an acid, the pigment must be acid resistant; if in contact with an alkaline environment, it must be alkali resistant. Colorants can be selected to either enhance or reduce electrical properties as desired. Toxicity may be a controlling factor, with FDA approval of the pigment being mandatory.

The following factors may be considered in the course of evaluating pigments : heat stability, lightfastness / weatherfastness, migration resistance, tinting strength, chemical resistance, blooming, dispersibility / dispersion behavior, behavior at low concentration, and plateout.

Some aspects of pigment behavior are not constant and will vary depending on heat history, dispersion technique, concentration, and other additives. If feasible, an evaluation program will be designed to examine these variables.

2.7.3 Applications for Pigments [23]

Pigments are used for the coloration of a very broad and diversified number of materials, and used for different applications may have the same chemical structures. However, their syntheses and their physical aftertreatments generally differ.

- surface-coating for interior, exterior, automotive and other applications,
- paints based on oleoresinous liquids and water emulsions,
- printing inks for paper (lithographic, rotogravure, and flaxographic systems) and for other materials (metal plates, foils, artists' and writing materials),
- coloration of plastics and rubber,
- textile printing,
- coloration of man-made fibers by mass pigmentation before fiber formation (dope dyeing), etc.

2.7.4 Organic Pigments [18, 24, 25]

Pigments can be classified according to a variety of criteria. The usual classification of pigments is according to chemical nature (inorganic, organic) and genesis (natural, synthetic). The subclasses of white, black, colored, luster, and luminescent pigments are also characterized.

Pigments are conveniently classified as either inorganic or organic. These two broad classes of pigments are of roughly comparable importance industrially. Table 2.3 presents the characteristics either inorganic and organic pigments.

Table 2.3 A comparison of the performance characteristics of inorganic and organic pigments [18]

Characteristic	Inorganic Pigments	Organic Pigments
Color Strength	Low	High
Color Brightness	Low	High
Opacity	High	Low
Transparency	Low	High
Lightfastness	Excellent	moderate – excellent
Heat Stability	Excellent	moderate – good
Solvent Resistance	Excellent	moderate – excellent
Chemical Fastness	Good – excellent	moderate – excellent
Cost	Low – moderate	moderate – high

As shown in Table 2.3, inorganic pigments generally are capable of providing excellent resistance to heat, light, weathering, solvents and chemicals and in those respects they can offer technical advantage over most organic pigments.

In addition, inorganic pigments are generally significantly lower in cost than organics. On the other hand, they frequently suffer from the disadvantage of considerably inferior intensity and brightness of color compared with organic pigments. Organic pigments are characterised in general by high color strength and brightness although they are somewhat variable in the range of fastness properties which they offer. There is, however, a range of high performance organic pigments offering excellent fastness while retaining their excellent color properties but these tend to be

rather expensive. The ability to provide opacity or to ensure transparency provides a further contrast between inorganic and organic pigments. Inorganic pigments are, in general, high refractive index materials which are capable of giving high opacity while organic pigments are low refractive index materials and consequently are transparent.

Moreover, for material to be colored, it is necessary that it absorbs light selectively within the range of the visible spectrum, i.e. light with wavelengths of about 400 – 750 nm. The colors of pigments are complementary to the color of the absorption bands, as shown in Table 2.4.

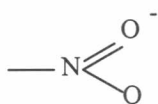Table 2.4   Relationships between light absorption and color [25]

Wavelength (nm)	Absorbed	Visible
400 - 435	Violet	Yellow - Green
435 - 480	Blue	Yellow
480 - 490	Green - Blue	Orange
490 - 500	Blue - Green	Red
500 - 560	Green	Purple
560 - 580	Yellow - Green	Violet
590 - 595	Yellow	Blue
595 - 605	Orange	Blue
605 - 750	Red	Blue - Green

As mentioned, the selection of colorant depends on such factors as the nature of the plastic, its processing, and its end use. The organic pigments suitable for coloring plastics can be displayed in Table 2.5.
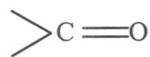
Pigments having a single, rather sharp absorption band will exhibit pure or clean color. It has been shown that for a compound to be colored it must contain a suitable unsaturated group called a chromophore. The presence of certain substituents in the molecules, known as auxochromes, has been found to strengthen and deepen the color. Commonly used chromophores and auxochromes are summarized below [11, 25] :

Chromophores :

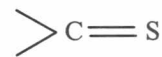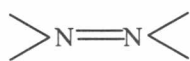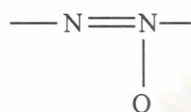$$-N = O \qquad -N\begin{smallmatrix} O^- \\ \\ O \end{smallmatrix} \qquad {>}C = O \qquad {>}C = S$$
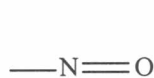
nitroso   nitro   carbonyl   thiocarbonyl
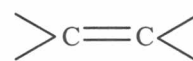
$${>}N = N{<} \qquad -N = N- \qquad -C = N- \qquad {>}C = C{<}$$
$$\qquad\qquad\quad | \qquad\qquad |$$
$$\qquad\qquad\quad O \qquad\qquad H$$

azo   azoxy   azomethine   ethenyl

$$-C_6H_5$$

phenyl

Auxochromes :

$$-N\begin{smallmatrix} H \\ \\ H \end{smallmatrix} \qquad -N\begin{smallmatrix} H \\ \\ CH_3 \end{smallmatrix} \qquad -N\begin{smallmatrix} CH_3 \\ \\ CH_3 \end{smallmatrix}$$

$$-OCH_3 \qquad -OH$$
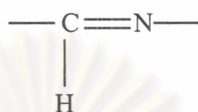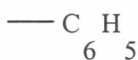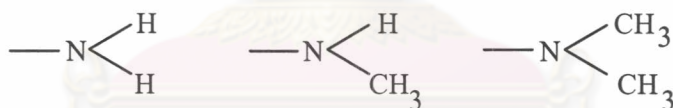
A molecule containing a chromophore but no auxochromes is called a chromogen and is not necessarily colored. In certain cases, however, an accumulation of chromophores in a molecule leads to the development of color without the presence of auxochromes, e.g. diacetyl, CH_3-CO-CO-CH_3, is yellow and azobenzene, C_6H_5-N=N-C_6H_5, is orange. The presence of resonating systems, i.e. conjugated systems, also enhances the color development due to the ready absorption in the visible range. Polymorphism can also produce differently colored crystalline forms, e.g. quinacridone exhibits red and violet polymorphic forms [25].

Table 2.5   Organic pigments suitable for coloring plastics [a] [21]

Color and Pigment Class	Resin Types	Heat Resistance Limitation[b] (^{o}F)
Blues, greens		
Phthalocyanines		
Blue	All resins except fluorocarbons and silicone molding compounds	425
Green	All resins except silicone molding compounds	450
Indanthrone blues	All polymers (except under reducing conditions)	400
Yellows, oranges		
Nickel-azo (green yellow)	Cellulosics, fluorocarbons, polystyrenes, flexible vinyls	375
Hansa Yellows (light yellow)	Amino resins, phenol-formaldehyde	250
Tetrachloroisoindolinones	All polymers except nylons	400
Disazo condensation pigments	All polymers	450
Benzimidazolones	All polymers	550
Flavanthrone Yellow	All polymers (except under reducing conditions)	400
Quinacridones	All polymers except nylon (slight solubility) and polystyrene (promotion of crystallization)	375
Perinone orange	Used widely as a shading colorant in all polymers	400
Reds, maroons, violets		
Lithol rubine (bluish red)	Polystyrene (general purpose)	300
Permanent Red 2B (Mn) (maroon, light red)	Cellulosics	350
Permanent Red 2B (Ca)	Flexible vinyls	350
Tetrachloroisoindolinones	All polymers except nylons	400
Disazo condensation pigments	All polymers	450
Benzimidazolones	All polymers	550
Quinacridones	All polymers except nylon (slight solubility) and styrene (promotion of crystallization)	375
Perylenes	All polymers	450
Dioxazine violets	All polymers; widely used for shading greenish phthalocyanine blue to reddish hue	375

[a] Acetal resin excluded from listing (individual colorants should be checked for application in this resin).

[b] Pigment should either not be used or should be used with extreme caution in polymers that are to be subjected to prolonged processing above the listed temperatures.

Organic pigments are divided into two major groups, the azo pigments and polycyclic pigments. A rough distinction can be made between azo and polycyclic pigments; the latter are also known as nonazo pigments. The commercially important group of azo pigments can be further classified according to structural characteristics, such as by the number of azo groups or by the type of diazo or coupling component. Polycyclic pigments, on the other hand, may be identified by the number and the type of rings that constitute the aromatic structure. Table 2.6 and 2.7 show the relation of visual color and chemical structure of each both pigments. Details of each pigment are presented as follows.

2.7.4.1 Azo Pigments [22]

Azo pigments, subdivided into the monoazo and disazo pigments (Table 2.6), have the azo group (-N=N-) in common. The synthesis of azo pigments is economically attractive, because the standard sequence of diazonium salt formation and subsequent reaction with a wide choice of coupling components allows access to a wide range of products.

Disazo Pigments

There is a dual classification system based on differences in the starting materials. The first and most important group includes compounds whose synthesis involves the coupling of di- and tetra-substituted diaminodiphenyls as diazonium salts with acetoacetic arylides (diarylide yellows, as demonstrated in Figure 2.5) or pyrazolones (disazo pyrazolones) as coupling components. The second group, bisacetoacetic arylide pigments, are obtained by diazotization of aromatic amines, followed by coupling onto bisacetoacetic arylides.

The color potential of disazo pigments covers the color range from very greenish yellow to reddish yellow and orange and red. Most show poorer lightfastness and weatherfastness; but better solvent and migration fastness than monoazo yellow and orange pigments. Their main applications are in printing inks and plastics, and to a lesser extent in coatings.

Table 2.6   Organic colored pigments : Azo pigments [26]

Chemical Structure	Blue	Violet	Red	Orange, Brown	Yellow	Yellow-Green	Green
Monoazo pigments				Monoazo orange pigments (also as lakes*)	Monoazo yellow pigments (also as lakes**)		
Disazo pigments				Diaryl yellow pigments			
Disazo pigments			Disazopyrazolone pigments		Bisaceto acetic acid arylide pigments		
Others			β-Naphthol pigments (also as lakes*)		Metal complex pigments**		
Others		Naphthol AS pigments (also as lakes*)					
Others		Naphthalenesulfonic acid pigments in lake form					
Others		Benzimidazolone pigments					
Others		Disazo condensation pigments					
Others				Isoindoline pigments			
Others				Isoindolinone pigments			

* Pigments in lake form are Me salts between sulfonic acid and/or carboxylic acid groups of dyes and metal salts

   (Me = alkaline earth, Na, Mn).

** Me complexes with azo or azomethine groups (Me = Ni, Co, Fe, Cu, Zn).
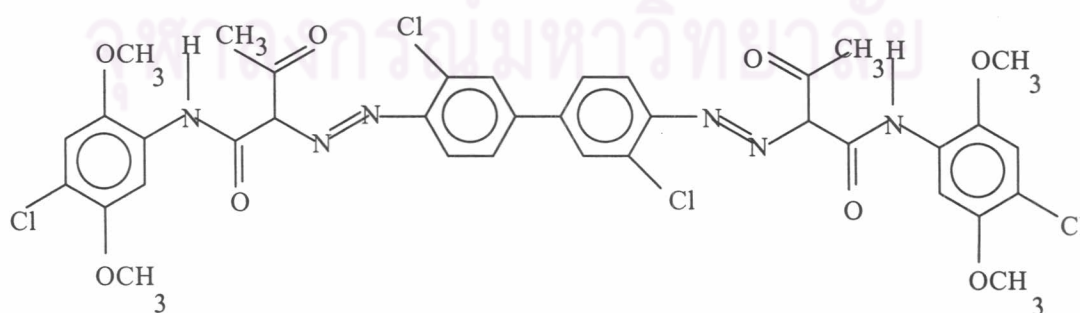

Figure 2.5   Chemical structure of diarylide pigment (PY 83) reddish yellow shade [22]

2.7.4.2 Polycyclic Pigments [22]

Pigments with condensed aromatic or heterocyclic ring systems are known as polycyclic pigments. The several pigment classes that fall into this category do not reflect their actual commercial importance; only few are produced in large volume. Their chief characteristics are good light- and weatherfastness and good solvent and migration resistance; but, apart from the phthalocyanine pigments, they are also more costly than azo pigments.

Table 2.7   Organic colored pigments : Polycyclic pigments [26]

Chemical Structure	Yellow-Green	Green	Blue-Green	Blue	Violet	Red	Orange, Brown	Yellow
Aromatic and Heterocyclic Pigments	Phthalocyanine pigments				Quinacridone pigments			
					Perylene pigments			
						Perinone pigments		
					Thioindigo pigments			
Anthraquinone Pigments	Triarylcarbonium pigments							Flavanthrone yellow pigments
					Pyranthrone pigments			Anthrapyrimidine pigments
					Dioxazine pigments	Anthanthrone pigments		Quinophthalone pigments

Aromatic or Heterocyclic Pigments

Phthalocyanine pigments are derived from the phthalocyanine structure as shows in Figure 2.6, a tetraazatetrabenzoporphine. Although this basic molecule can chelate with a large variety of metals under various coordination conditions, today only the copper(II) complexes are of practical importance as pigments. Excellent general chemical and physical properties, combined with good economy, make them the largest fraction of organic pigments in the market today. Copper phthalocyanine blue exists in several crystalline modifications. Commercial varieties include the reddish blue alpha form, as stabilized and nonstabilized pigments; the greenish blue beta modification;

and, as yet less important, the intense reddish blue epsilon modification. Bluish to yellowish shades of green pigments may be produced by introduction of chlorine or bromine atoms into the phthalocyanine molecule.
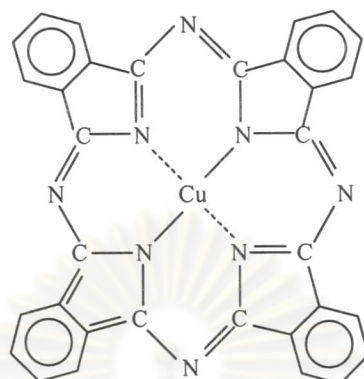

Figure 2.6 Chemical structure of phthalocyanine pigment (PB 15) reddish blue shade [11]

The quinacridone structure is a linear system of five anellated rings, like was depicted in Figure 2.7. These pigments perform largely like phthalocyanine pigments. Outstanding light and weather fastness, resistance to solvents and migration resistance justify the somewhat higher market price in applications for high grade industrial coatings, such as automotive finishes, for plastics, and special printing inks. Unsubstituted trans-quinacridone pigments are commercially available in a reddish violet beta and a red gamma crystal modification. One of the more important substituted pigments is the 2,9 -dimethyl derivative, which affords a clean bluish red shade in combination with excellent fastness properties. Solid solutions of unsubstituted and differently substituted quinacridones and blends with quinacridone quinones resulting in reddish to yellowish orange pigments are commercially available; while 3,10-dichloroquinacridone as yet enjoys only limited success as a pigment.
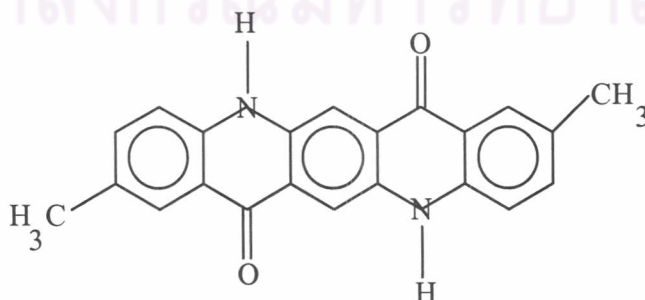

Figure 2.7 Chemical structure of quinacridone pigment (PR 122) bluish red (magenta) shade [22]

2.8 Medium Density Polyethylene

Polythene is the accepted abbreviation for the chemical name, polyethylene. This is the least complex of all the synthetic plastics, containing only carbon and hydrogen, linking on polymerization into a simple linear carbon-hydrogen chain [1].

Ethylene   polymerized into   Polyethylene
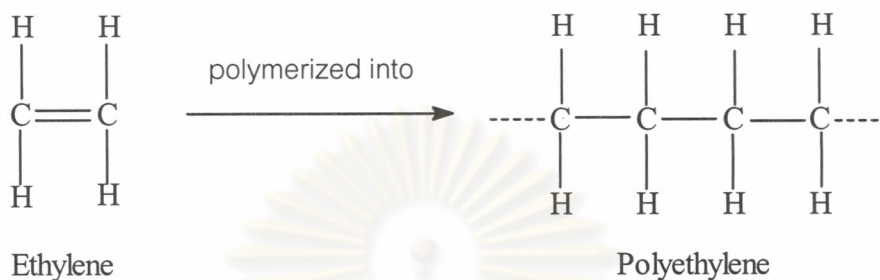
Polyethylene (PE) is used more than any other thermoplastic polymers. There is a wide variety of grades and formulations available that have an equally wide range of properties. In general, the outstanding characteristics of polyethylene are : toughness, ease of processing, chemical resistance, abrasion resistance, electrical properties, impact resistance, low coefficient of friction, and near-zero moisture absorption [27]. Thus, PE is one of the most versatile of plastics [28] and easily molded by the following standard processes : injection molding (for most household goods including buckets, bowls, toys, novelties); extrusion (for sheets, films, tubes, plastic bags, cable insulation or in packaging); vacuum forming, blow molding (for most squeeze bottles, milk bottles and liquid containers); and rotational molding, which is like blow molding but used for large containers such as drums and furniture. The disadvantages of polyethylene are that it has a low softening point (80 – 130 $^\circ$C), it scratches easily, and it can suffer from stress cracking [1]. Processing temperatures range from 160 to 340 $^\circ$C [10].

Polyethylene with repeating unit structure of $[CH_2CH_2]_n$ is produced by the polymerization of ethylene [29]. Polyethylene is roughly classified by the density (grams per cc) as shown below [30].

Very low density polyethylene (VLDPE)	0.890 - 0.910
Low density polyethylene (LDPE)	0.911 - 0.925
Medium density polyethylene (MDPE)	0.926 - 0.940
High density polyethylene (HDPE)	0.941 - up

Many resins are available for molding plastic containers. Table 2.8 illustrates the comparative properties of polyethylene with other common resins. These resins are available in several grades that can alter and modify its properties [31].

Table 2.8   Properties of common resins [31]

Requirement	PE	PP	PET	PC	COC	PEN
Lightweight	2	1	5	6	3	5
Clarity	3	2	1	1	1	1
Toughness	1	3	2	3	5 - 7	2 - 7
Water Absorption	2	2	3	6	1	3
H_2O Permeation	2	2	4	7	1	3
CO_2 Permeation	6	5	2	9	6	2
O_2 Permeation	7	6	2	8	7	2
Acid Resistance	2	2	4	4	2	3
Alkali Resistance	2	2	3	7	2	2
Oil Resistance	4	3	2	4	5	2
Solvent Resistance	3	3	2	6	3	2
Resistance to high humidity	1	1	1	6	1	1
Resistance to sunlight	4	4	1	4	1	1
Heat Resistance	3	2	3	1	1	1
Cold Resistance	1	4	2	1	5 - 7	2 - 7

Remarks   -   PE : Polyethylene, PP : Polypropylene, PET : Polyethylene terephthalate, PC : Polycarbonate, COC : Cyclic olefin copolymer, and PEN : Polyethylene naphthalate

-    1 = best, 9 = worst

-    This table is provided only as a guide. Actual compatibility of the resin and the product is the responsibility of the product manufacturer.

Medium density polyethylene (MDPE) is made by combining low density and high density polyethylene during the manufacturing process [32], so it provides intermediate properties between low and high density polyethylene. It is useful for squeeze containers, where more rigidity and hardness than LDPE and less rigidity and hardness than HDPE is required [31]. MDPE is a tough, semi-transparent material, and better mechanical properties than LDPE [32]. It has good welding properties, and can be welded at 130 - 160 °C. Comparing to LDPE, MDPE has lower in permeability of

aqueous vapours and gases like oxygen. It has a good shock and drop resistance. Notch sensitive of MDPE is less, however, it is better in stress cracking resistance compared to HDPE [33].

Polyethylene is not difficult to color. Both inorganic and organic pigments are suitable. The method chosen will depend on the equipment and level of technology of the processor. If individual pigments are purchased, they must be blended to produce the exact color desired. A more economical method is to purchase a mixture of dry colors, preblended to give a certain shade. Then, minimum color technology which may be led to contaminate, is required to the points of user. There is little flexibility to adjust the process variables. Color additives may contaminate the user's polymer, and the final shade which was produced, may be varied with equipment or with the size and shape of the resin particles [10]. The respective processing temperatures are determined the criteria for pigment selection. At any given temperature, the flow property of a system is defined by the density and the molecular weight of the plastic and characterized by the melt flow index [22].

2.9 Rotational Molding

2.9.1 Introduction [3]

Rotational molding, also known as rotomolding or rotocasting or rotoforming [2, 34, 35], is a process for manufacturing hollow plastic parts especially in large and uncomplicated products. In recent years, it has become a realistic alternative to injection and blow molding techniques since it produces hollow articles with very low residual stresses, no weld lines, good wall thickness distribution, and no tops and tails or sprues and runners to remove and recycle.

The concept of rotational molding originated with liquid poly(vinyl chloride) (PVC) plastisols in a process called slush molding. However, the process only developed slowly because of the lack of other suitable materials. Powdered thermoplastics have been extensively rotationally molded since about 1960 [4, 6]. But it was not until the early 1960s that a suitable grade of polyethylene (PE) powder was introduced [3]. After that time the process developed steadily, and today it has an annual growth rate of 10 to 15%. Currently, powdered polyethylene still accounts for the highest tonnages processed, for more than 85% of the volume in rotational molding because of its acceptable processability, good thermal stability and good mechanical properties [8], while PVC plastisol is used less and less. Other materials suitable for rotational molding are processed in relatively small quantities. These include crosslinkable PE, nylons, polycarbonate, polyester elastomers, polypropylene, ethylene vinyl acetate, ethylene butyl acrylate, fluoropolymers, and the polyurethanes. Because of recent technological changes and innovations in the polymer industry, rotational molders are seeking resins that can be processed at shorter cycle times or can provide better properties than incumbent polyethylenes [8].

The work of Chaudhary, Takacs, and Vlachopoulos in 2002 [8], was resulted in faster bubble removal, more uniform thickness and shorter cycle times. These were then evaluated the effect of blending minor amounts of an ethylene styrene interpolymer which made by INSITE (Trademark of The Dow Chemical Company) Technology, or ethylene vinyl acetate (EVA) copolymers which have a differing in vinyl acetate contents, with polyethylene. The effects on cycle times and impact strength in rotational molding,

were observed. Blending interpolymer or EVA with polyethylene resulted in improved environmental stress cracking resistance and decreased flexural modulus. Besides two years ago (2001) [7], they have studied the effect of low molecular weight additives as sintering enhancers for PE, to validate the results in rotational molding on mechanical properties. The following additives were blended with linear low-density polyethylene : mineral oil, glycerol monostearate and pentaerythritol monooleate. The use of additives, especially mineral oil, resulted in shorter cycle time without sacrificing peak impact strength.

In addition, rotational molding is a difficult process to model due to the complexities caused by the biaxial rotation of the mold, the physical and phase changes which take place in the plastic, and the dynamic nature of the boundaries within the mold. Thus, the works in cooperation of Crawford in 1989 with Nugent [36], in 1993 with Sun [37], and in 1994 with Xu [38] were studied in computer-simulation to mend the problems and to predict the output of the rotational molding process. Comparison of the output from the simulation with experimental results shows that the software can give accurate predictions of oven time and cycle time. Furthermore, the effects of mold shape, mold size, powder particle shape, material physical properties, oven temperature, room temperature, cooling temperature, internal heating and internal cooling on oven time and, cycle time can be examined by the software [37].

2.9.2   Materials [14, 39]

A variety of materials is available. The most widely used are polyethylenes and plastisols. The majority of rotationally molded products are produced by polyethylene. This polymer can be molded in three main types of density that are low density (LD), medium density (MD), and high density (HD). Medium density is the most popular grade of material with a typical density of 0.935 g cm^{-3}. The material has high impact strength and is resistant to a wide range of chemical substances.

Food grade polyethylene is available as flame retardant and high UV resistant grades. Polypropylene can also be rotationally molded for applications that require a material with higher heat resistance. Polyurethane are more expensive and require specialist machinery to produce. Other materials include cross-linkable polyethylene,

nylon, fluoropolymers, cellulose acetate butyrate, elastomers, polycarbonate, ionomer, EVA, and specially formulated compounds.

2.9.3 Process [40, 41]

The four-phase rotational molding process has been concluded to exhibited in Figure 2.8, as follows.

(a) Charging : Pre-measured plastic resin is loaded into the mold.

(b) Heating : As closing the mold, the mold is placed into an oven, and slowly rotated on two axes. The heat penetrates the molds, melting resin adheres to the mold's inner surface until it is fused and evenly coats the entire surface.

(c) Cooling : During this phase, the mold continues to be rotated to maintain even walls as air, water spray, or a combination of the two gradually cools the mold.

(d) Demolding : The mold is opened, the finished part finally removed, and the mold is ready for its next cycle.

In rotational molding, shortening the cycle time is one of the most important requirements for increasing production rates and reducing product cost. A characteristic feature of the process is that the mold and plastic powder are heated from room temperature to the melting temperature of the plastic and then back to room temperature. In addition, in the vast majority of cases the heat input and subsequent heat extraction occur at the outside surface. In order to improve the heat transfer, the work of Sun and Crawford in 1993 [3] considered the effects of internal heating and cooling. A mathematical model has been developed in which an internal heating term can be incorporated. The experiments with rotational molding powders showed that the predictions made by the model were accurate. In particular, it was found that the introduction of internal heating was very effective in shortening the cycle time and that the introduction of internal cooling in rotational molding provided a more uniform structure and less likelihood of warpage.
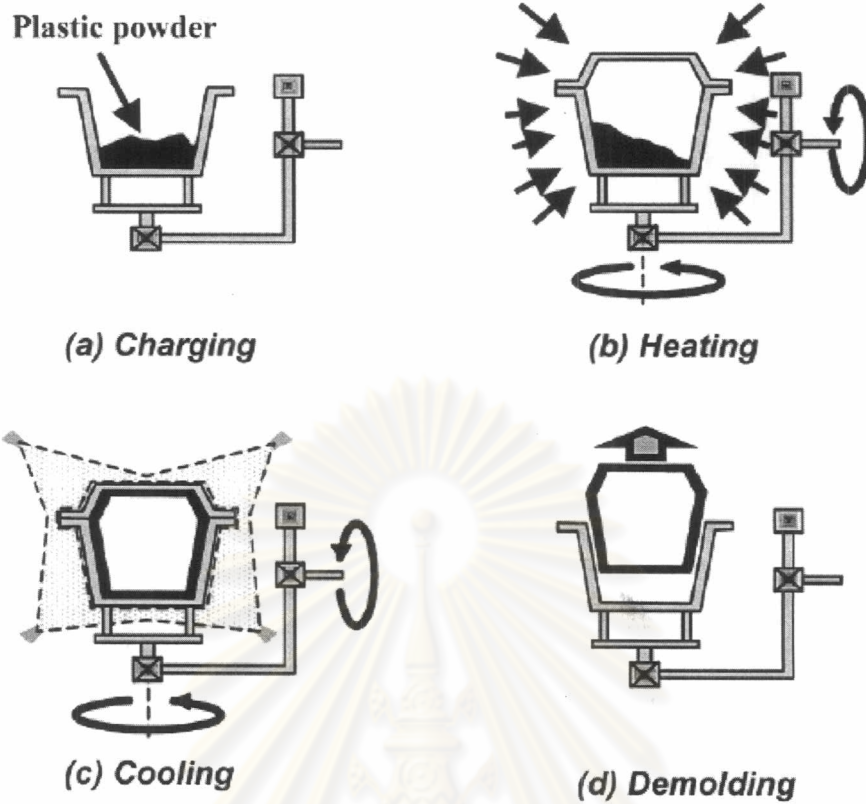
Plastic powder

(a) Charging

(b) Heating

(c) Cooling

(d) Demolding

Figure 2.8   The four-phase rotational molding process [41]

2.9.4   Products [39]

With rotational molding, parts can be molded economically in a variety of shapes and sizes, many of them are difficult to produce by any other process.   Industrial and commercial products in the agriculture, health and science, or point of sale areas include specialty tanks and containers for fuel, water and chemical processing, livestock feeders, drainage systems, food service containers, instrument housings, fittings, medical equipment, safety helmets, vending machines, highway barriers and road markers.   Consumer products in the recreational, special application, toy and transportation areas include boats, kayaks, child care seats, light globes, tool carts, tables, planter pots, youth beds, playing balls, playground equipment, headrests, truck / cart liners and air ducts.

2.9.5 Advantages and Disadvantages [2, 3, 5, 7, 8, 13, 14, 34, 35, 39 - 44]

The advantages and disadvantages of the rotational molding are listed as follows.

1. Molds are simple and tooling costs are very low; the forces involved in rotational molding are small, and cheap molds are satisfactory. The plant is also cheap by comparison with other molding processes;

2. Rotational molding is a shear-free and pressure-free process;

3. Products are characterized by :

    1) hollow articles without seams

    2) zero orientation; there is no shearing at all during processing and dimensional stability is therefore excellent

    3) virtually no internal stresses, very low residual stresses, no weld lines, and no ejection marks

    4) very high physical properties-equal to those published in suppliers' technical service notes, which most processes do not achieve. Rotationally molded bins and traffic cones are exceptionally tough

    5) excellent load-bearing properties

    6) resistance to stress-cracking and corrosion

    7) uniform wall thickness no thinning in the extremities, compared with blow molding or thermoforming, especially in corners

    8) wide range of part-sizes and thicknesses on same equipment. Thickness can range from 1/16 to $\frac{1}{2}$ inches but not suit for the thickness below 0.75 mm.

    9) no tops and tails or sprues and runners to remove and recycle, minor undercuts are possible with no draft angles required

    10.) design flexibility from small and intricate to large and complex, fine detailling and textures are easy to achieve. Very large and flat areas are quite difficult to mold.

    11.) variety of finishes and color

    12.) metal inserts as integral parts

4. The method is capable of more complex shapes than are possible by blow molding, but not for sharp-cornered shapes.

5. Flexibility to have more than one material in a part, ability to produce multi-wall moldings, hollow or foam filled, when multi-layer extrusion blow molds are not justified

6. Allows "molded-in" threaded inserts, either on the same plane as the mold parting line or at 90°

7. Economical for short production runs, prototype research and volume production

8. One-piece construction : virtually stress-free enclosed parts or with openings

9. In general, the process is labour and material intensive, especially if multiple parts are molded in one cavity and have to be separated.

10. Short lead-time while the process is long cycle times, which are significantly affected by the sintering rates of thermoplastic powder. The cycle times can vary from five minutes to one hour depending on the material used, the wall thickness and the machinery involved.

11. Not acceptable for all plastics

Researchs of rotational molding regarding the problems such as bubble, warpage, and shrinkage in outputs which have been carried out. For example, Chen, White, and Ohta in 1990 [4] demonstrated the mold pressurization in process of rotationally molded polyethylene parts. It was shown that relatively low pressurization of molds substantially reduced the warpage of molded polyethylene parts. Samples cut out of parts produced in pressurized molds had the same density distributions, Izod impact, and uniaxial stress-strain characteristics as parts fabricated in unpressurized molds. As was shown in their earlier studies [4], warpage in rotationally molded parts is associated with residual quench stresses associated with non-uniform densification due to rapid cooling coupled with easy separation of solidified parts from mold walls. Mold pressurization is found not to influence density distributions through the thickness of molded parts or the mechanical properties of molded parts.

Four years later (1994), Bawiskar and White [6] studied the warpage, global shrinkage, residual stresses, and mechanical behavior of rotationally molded parts

produced from different polymers. It is the purpose of this study to make an investigation comparing warpage levels developed in parts produced from seven different thermoplastics including polyethylenes of differing density, polypropylene, polyamide-6, polycarbonate, and polystyrene. Five of these thermoplastics are crystalline and two are glasses. Generally, warpage, global shrinkage, and residual stresses increase with increasing quench rate for all the polymers. Further, the levels of warpage and global shrinkage increases with extent of crystallization, i.e., products from glassy polymers exhibit little warpage and those from highly crystalline polymers are highly warped. Increasing rate of quench tends to increase elongation to break and impact strength. These confirm the considerations of theirs earlier papers [4].

Afterwards, in 1999, Kontopoulou and Vlachopoulos [35] studied the bubble dissolution in the rotational molding process and reported that bubble dissolution depends significantly on initial bubble size, surface tension, and air concentration in the polymer melt, but it is not influenced considerably by melt viscosity when the latter lies within ranges typical for rotational molding resins. The application of pressure after the polymer has melted leads to a significant acceleration of the dissolution rate, owing to an increased driving force for diffusion.

Recently, in 2001, Oliveira and Cramez [45] found that the rotational molding is not favorable for the dispersion of additives like pigment. In the rotational molding of semicrystalline polymers, the slow heating, cooling rates, and an almost absence of shear stresses were led to a coarse spherulitic morphologies free from molecular orientation. The morphology is affected by the way the nucleating pigments are incorporated during the mixing process. For example, the poor mixing capability of turboblending leads to the pigment concentrating around the polymer particles and to the development of transcrystalline textures. Conversely, the more effective extrusion compounding allows the pigment to disperse and distribute better and leads to the reduction of the spherulite size. An improvement of the impact strength is achieved only if the finer morphology is associated with a significantly lower degree of crystallinity.

2.10 Compression Molding

2.10.1 Introduction [5, 46 - 49]

Compression molding is the oldest mass production process for polymer products, a forming process similar to making a waffle. The molding process can be carried out with either thermosets or thermoplastics. However, it is almost exclusively used for thermosets and is not generally used for thermoplastics. The only important product to use a thermoplastic in compression molding is the long playing gramophone record in black PVC copolymer. The main reason for this choice of process in this case gives a clue to one of the features of the process, namely, the low level of orientation in the moldings. It is difficult to produce thin, flat discs like gramophone records by injection molding without warping; the orientation leads to distortion to a dished shape or a saddle shape, both clearly quite unacceptable in this product. Compression molding delivers the flat records which have been so successful for over 50 years, although now being overhauled in the market by the compact disc which is in fact injection molded. The materials that form the main users of the compression molding technique are the thermosetting resins and vulcanizable rubber.

2.10.2 Process [5, 49]

The principle of the compression molding process can be outlined as follows.

1) The mold is held between the heated platens of a hydraulic press;

2) A prepared quantity of molding compound is placed in the mold, usually by hand, and the mold placed in the press;

3) The press closes with sufficient pressure to prevent or minimize flash at the mold part line;

4) The compound softens and flows to shape; the chemical cure then occurs as the internal mold temperature becomes high enough;

5) If necessary, cooling takes place, although for the vast majority of thermosets this is not needed;

6) The press is opened and the molding removed. Frequently, the mold is removed from the press and opened on the bench to extract the molding. It is reloaded with a fresh charge before returning it to the press to commence another cycle.

Compression molding is simply the squeezing of a material into a desired shape by application of heat and pressure to the material in a mold. The three compression molding factors – pressure, temperature and time the mold is closed – vary with the design of the finished article and the material being molded.

2.10.3 Advantages and Disadvantages [5, 47, 50]

1. Relatively low capital investment and tooling costs
2. Labor intensive
3. Short cycle time
4. High volume production
5. Low orientation in the moldings
6. Low residual stresses in product
7. Retainable mechanical and electrical properties (because there is little shearing flow to cause tracks)
8. Class A (high quality) surfaces
9. Low scrap arisings (2–5%, but it must be remembered, irrecoverable)
10. Secondary operations are sometimes required
11. Low mold maintenance (There is little erosion from the low shear forces.)

2.11 Extrusion [5]

2.11.1 Introduction [49, 51]

Extrusion molding is the method employed to form thermoplastic materials into continuous sheeting, film, tubes, rods, profile shapes, and filaments, and to coat wire, cable and cord. In principle, the extrusion process comprises the forcing of a plastic or molten material through a shaped die by means of pressure. The process has been used for many years for metals such as aluminium which flow plastically under deforming pressure. The earliest form of extrusion process for polymers similar ram-driven machines were used. In the modern process, however, screws are used to progress the polymer in the molten or rubbery state along the barrel of the machine. The most widely used type is the single screw machine. Twin screw extruders are also used where superior mixing or conveying is important. The machine consists essentially of an Archimedian screw fitting closely in a cylindrical barrel, with just sufficient clearance to allow its rotation. Solid polymer is fed in at one end and the profiled molten extrudate emerges from the other. Inside, the polymer melts and homogenizes.

Twin screw extrusion is used extensively for mixing, compounding, or reacting polymeric materials. The flexibility of twin screw extrusion equipment allows this operation to be designed specifically for the formulation being processed. For example, the two screws may be corotating or counterrotating, intermeshing or nonintermeshing. In addition, the configurations of the screws themselves may be varied using forward conveying elements, reverse conveying elements, kneading blocks, and other designs in order to achieve particular mixing characteristics.

There is a research which was concerned to extruder, as work of Mielcarek, D.F. in 1987. He reported about the versatility and benefit of twin-screw compounding. The twin-screw extruder is a versatile tool, capable of handling a wide range of applications. In addition, its inherent shear, conveying, feeding and mixing characteristics have made it the machine of choice for the majority of today's sophisticated requirements. 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.

2.11.2 The zones in an extruder

1. Feed Zone

In the first zone, usually termed the "feed" zone, the function is to preheat the polymer and convey it to the subsequent zones. The screw depth is constant and the length of this zone is such as to ensure a correct rate of feed forward, neither starving it nor overfeeding. This varies somewhat for optimum performance with different polymers.

2. Compression Zone

The second zone has decreasing channel depth. There are several functions for this zone, usually called the "compression" or "transition" zone. Firstly, it expels air trapped between the original granules; secondly, heat transfer from the heated barrel walls is improved as the material thickness decreases; thirdly, the density change during melting is accommodated. Again, there is variation in the ideal design for each polymer type.

3. Metering Zone

The function is to homogenize the melt and hence to supply to the die region material which is of homogeneous quality at constant temperature and pressure.

2.11.3 Categories of Twin Screw Extruders

Twin screw extruders divide into co-rotating and counter-rotating types. As the names indicate, the difference is in whether the two screws rotate in the same or in opposite directions, i.e. both clockwise or counterclockwise, or one in each sense.

The next division is determined by whether the two screws mesh with each other or not; they are described as meshing or non-meshing. The non-meshing types consist of essentially two single screws side by side and work in a similar manner to single screw machines; they are not true twin screws and are better described as "double screws". Within the meshing (or intermeshing) types, there is a further subdivision into

conjugated and non-conjugated machines, depending on whether the meshing flights fully occupy the channels in the meshing area.

2.11.4 Process [49]

1. Dry plastic material is first loaded into a hopper.
2. Then, it is fed into a long heating chamber through which it is moved by the action of a continuously revolving screw.
3. At the end of the heating chamber the molten plastic is forced out through a small opening or die with the shape desired in the finished product.
4. As the plastic extrusion comes from the die, it is fed onto a belt conveyor where it is cooled, most frequently by blowers or by immersion in water.