CHAPTER II
A REVIEW BACKGROUND OF CARBON BLACK

2.1 Structure of Carbon Black

Carbon black, the prominent reinforcing filler for rubber, is also widely used in plastics for coloring, UV protection, and electrical conductivity. It is a colloidal form of carbon, generally consisting of irregularly shaped units (fused aggregates of particles) of submicrometer dimensions, which adhere to each other via van der Waals forces. Carbon black is more difficult to disperse than most other additives [Donnet and Voet (1976)].

2.1.1 Microstructure

Within each aggregate the carbon atoms are arranged in imperfect graphitic layers. High resolution transmission electron microscopy demonstrates that the layers are arged more or less concentrically within each particle , with a fair degree of parallelism between adjacent layers in small regions [Oberlin et. al. (1972)]. However, the layers are not arranged as in graphite, and the average interlayer spacing in carbon black is about 3.5-3.65 Å, compared with 3.345 Å for graphite.

2.1.2 Particle Size

In carbon black terminology the term "particle" refers to the spherical nodules of which the aggregates are composed, as shown in electron micrographs and particle size refers to their diameter. It is important to realize

that (except for some thermal blacks of large particle size) individual particles are not found in carbon blacks whether in the dry state or after dispersing in a
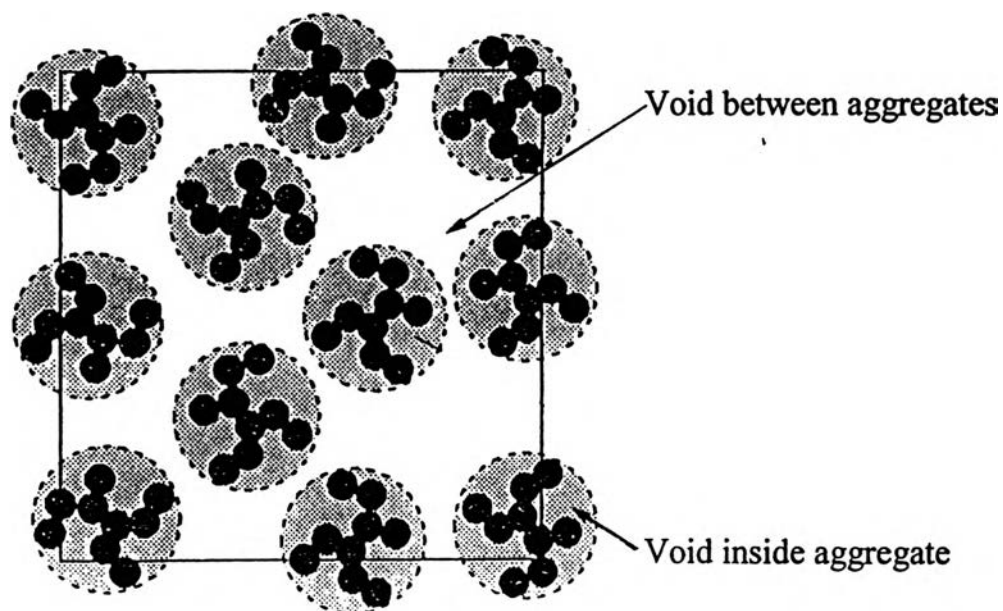
(a). High structure carbon black
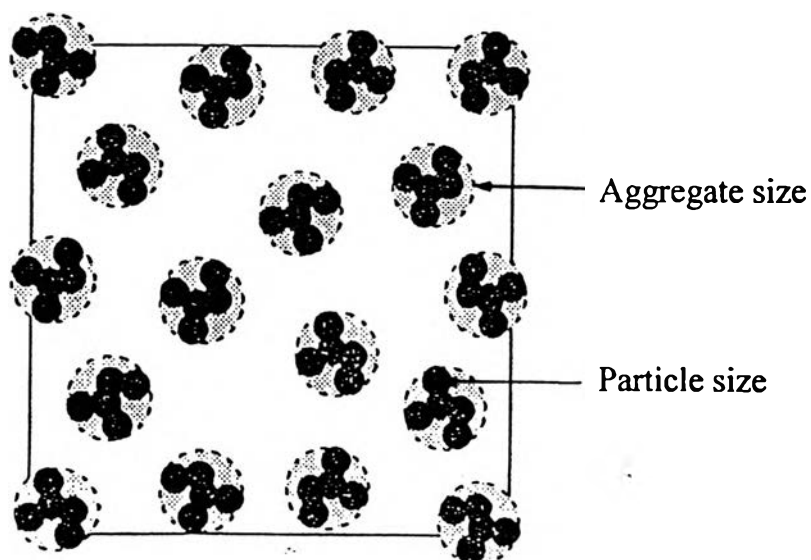
(b). Low structure carbon black

Figure 2.1 Structure of carbon black: (a) High structure carbon black

(b) Low structure carbon black [Hiroshi (1997)].

polymer, hence, the *aggregate* is the smallest "particle" unit. Nevertheless the particle concept is meaningful for the properties of the carbon black. Since the particles are visible in electron micrographs, measurement of particle size can be made directly using SEMs and TEMs. Generally, Transmission Electron Micrographs (TEMs) are used because of their high resolution. Unfortunately there are some difficulties in measuring particle sizes precisely by these methods, such as (1) the particles are not perfectly spherical; (2) the particles are connected to one another by "necks"; and (3) many particles are not seen in TEMs or in Scanning Electron Micrographs (SEMs) of an aggregate because they are hidden by other particles of the same aggregate. Particle size measurements are especially useful for calculation of the distribution of particle size and various mean diameters and refined methods have been developed for such calculations [Medalia and Heckman (1971)].

2.1.3 Surface Area and Porosity

The specific surface area is the surface area of a sample divided by its weight. The surface area may be determined by adsorption of a gas for example, by adsorption of nitrogen at liquid nitrogen temperature. Measurements may be made at several partial pressures and the calculation carried out according to the Brunauer-Emmett-Teller (BET) equation; or for rapid results a single data point (e.g., at a partial pressure of 0.15 atm) may be used [ASTM (D3037)]. Some carbon blacks, especially those of very high surface area (used for applications that need intense jetness or high electrical conductivity) may contain micro and mesopores in which substantial amounts of the gas can be adsorbed [Nakajima and Harrell (1984)]. These pores tend to be slit-shaped, since they are formed by burning of layer planes. The external surface area can be distinguished from the total surface by the *t* method

[Nelson (1986)], in which the sample is covered with a monolayer of adsorbed gas, thereby also filling the pores, and the amount of gas required to put on the *second* layer is then measured. Adsorption of iodine under controlled conditions gives the *iodine number* [ASTM (D1510)], which is approximately equal to the specific surface area. Cetyl trimethylammonium bromide (CTAB) is a bulky molecule that is adsorbed from aqueous solution to give a CTAB Surface area [ASTM (D3765)]. This is a good measure of the external surface area, and is little affected by surface chemistry; however, the procedure is more difficult to carry out and less precise than those for the determine iodine number.

2.2 Carbon Black Aggregate and Aggregate Behavior

The principle result of the aggregated nature of the carbon black entities is to impart a bulkiness considerably higher than that of individual spheres. The bulkiness is the ratio of the effective volume of the aggregates to their true volume. In many grades of carbon black the aggregates have a densely packed core and the morphology becomes more open toward the periphery.

2.2.1 Aggregate Morphology

The bulkiness of carbon black, traditionally referred to as "structure" is measured by adsorption of dibutyl phthalate (DBP) in a two-bladed mixing machine that senses the end point as a sharp increase in viscosity, so - called DBPA (dibutyl phthalate adsorption) value [ASTM D2414]. Figure 2.1 represents high structure carbon black and low structure carbon black. DBPA below 70 is defined for low structure carbon black and over 90 for high structure carbon black. Structure can also be measured from

the density of the black under a definite pressure, such as 25000 psi; however, this method requires precisely controlled conditions and has not found widespread use.

The aggregate size distribution can be measured by centrifugal sedimentation, spectral extinction, electron microscopy, small-angle-X-ray scattering, field flow sedimentation, and other methods [Janzen (1982)].

2.2.2 Interaggregate Interaction

Carbon black aggregates are anisometric, with an average anisometry (by electron microscopy) of about 1.8 for most grades. Recently it has been found possible to characterize aggregated materials, including carbon black, by fractal dimensions. Measurements have been made in various ways on electron micrographs and by other techniques [Ehrburger-Dolle et al. (1990) and Gerspacher et al. (1991)], and investigators are attempting to apply the fractal concept as an aid to understanding the effect of carbon black on rubber and plastic compounds.

Carbon black aggregates interact with each other, mainly because of van der Waals forces, and perhaps partly because of interaction of acidic groups on aggregates with basic groups or the graphitic layer surface. In the process of dispersing carbon black in polymer, the agglomerates (fused aggregate of particle) are broken down and the aggregates become more or less separated from one another. At normal loadings of carbon black in rubber, the aggregates form a network, with many interconnecting paths. In these paths the carbon surfaces of adjacent aggregates are not necessarily in direct contact but may be separated by a thin layer of polymer. The existence of this network is shown both by electrical conductivity and by the decrease in elastic modulus with increasing strain amplitude (Payne effect) [Kraus (1984)].

Interaggregate interaction is also thought to be involved in the formation of strands of aggregates that occurs when a black-filled rubber compound is stretched. These strands, whose existence is shown by a large increase in electrical conductivity in the direction of stretching, are thought to be responsible for reinforcement, in the sense of providing an increase in ultimate properties such as tensile strength [Medalia (1987)].

2.2.3 Incorporation and Dispersion

The first step in mixing is "incorporation", by which the carbon black becomes included within the polymer matrix; alternatively, this step may be viewed as replacement of air within carbon black pellets or agglomerate by polymer. The incorporation time (the time required to eliminate essentially all the loose, dry black from a mix), which comes approximately at the second peak(power curve i.e., a plot of torque versus mixing time) is affected principally by the structure (or DBP adsorption of the black) and also by the bound rubber formed during incorporation. Higher structure was found to give shorter incorporation time, in contrast to earlier statements claiming the opposite effect; while higher bound rubber led to longer incorporation times [Cotten (1984), (1985)].

Dispersion involves breakdown of the pellets to individual aggregates or small agglomerates (clusters of aggregates) . Breakdown may involve both fracture and peeling [Shiga (1985)]. Incomplete breakdown, leaving rubber-filled pellet fragments larger than a few micrometers, is harmful to the ultimate properties of the rubber compound such as tensile strength and abrasion resistance [Hess (1991)]. The agglomerate dispersion is measured by various conventional dispersion tests based on examination of microtomed sections or on the roughness of cut surfaces [ASTM (D2663)]. The net effect of dispersion and flocculation is to form a three-dimensional

network of carbon black aggregates and clusters. As pointed out above, improved "separation dispersion" gives lower electrical conductivity and lower mechanical hysteresis; thus this type of dispersion can be estimated by measuring either of these properties [Cembrola (1983)]. The time to attain satisfactory dispersion, once the carbon black has been incorporated, as seen in the case of high structure carbon black , will be more required , since the aggregates of high structure carbon black are packed tightly. Hence, high structure aggregates are more difficult to disperse than low structure aggregate [Cembrola (1983)].

A significant fraction of rubber, especially synthetic rubbers, is marketed in the form of carbon black masterbatches, prepared by mixing the carbon black with latex or a solution of rubber prior to coagulation or removal of solvent. In latex masterbatches the carbon black is incorporated but not well dispersed. These masterbatches are stiff and require a high initial power consumption but give shorter dispersion times and give excellent final dispersion with less work require on the compound.

2.3 Carbon Black Dispersion

Most of the studies relating the state of dispersion to the properties of compounds use microscopic techniques and determine the average diameters of the agglomerates [Tovmasyan (1983), (1989)], the number of agglomerates greater than a certain size [Nishio and Kitadono (1989)], the fraction of agglomerates [Suetsugu (1989), Yabuta and Sakaki (1990), Nakao et al. (1992), Suetsugu (1990), Tovmasyan et al. (1983, 1989), Nishio and Kitadono (1989), and Svehlova and Poloucek (1990)], and so on.

2.3.1 Carbon Black in Plastics

Carbon black is used in plastics for coloring (tinting and jetness), for protection against sunlight (UV attack), thermal aging, and for electrical conductivity. Typical concentrations are of the order of 0.5-3%. Higher concentrations render the compound more brittle, especially when blacks of smaller particle size are used, and adversely affect the tensile (yield) strength and elongation at break. However, to obtain satisfactory dispersion, the carbon black is frequently mixed into the plastic at a higher concentration (and thus giving a higher melt viscosity) and is then "let down". This masterbatch technique by loose carbon black pellets would present a problem. For electrical conductivity, the concentration of black must be high enough to form a network. The concentration of carbon in a masterbatch may be from 5% to above 35% depending on the grade of black and the degree of conductivity desired [37]. Tinting by carbon black refers to imparting a gray color to a compound made with a white pigment; or more generally to darkening of the color produced by another pigment. The tinting strength of a particular carbon black (i.e., the amount of carbon black required to impart a certain degree of darkening or grayness) depends on the absorbance at a given wavelength and is a function of the amount of carbon per aggregate.

2.3.2 Mixing Process and Dispersion State

To understand the correlation between the mixing process and compound properties it is important to characterize the phase morphology. Many procedures have been used through the years to characterize the level of dispersion of fillers. These include optical microscopy [Manas-Zloczower et al. (1982)], electron microscopy, surface roughness, electrical [Suetsugu (1989), Yabuta and Sakaki (1990), and Nakao et al. (1992)], and small-angle light scattering [Suetsugu (1990)].

The microscopy methods give only qualitative information unless subjected to extensive quantitative evaluation. The surface roughness method seems to have been applied only to particle-filled elastomers, with ambiguous results. Electrical conductivity measurements are a useful measure of dispersion in conductive filler compounds, though difficult to interpret.

Another measure of dispersion may be defined based on the fraction of agglomerates [Suetsugu (1990)]. The compound is carefully microtomed for scanning electron micrographs made at low magnification.

In the Quadrat method and Tovmasyan's method [Tovmasyan et al. (1983)], the particles must be counted to obtain the indices. These methods are useful when the size of agglomerates is comparable to the individual particle size, or when the size distribution of the dispersed phase is relatively narrow. In other cases - that is, when thousands of particles form a single dispersed phase much greater than individual particles, or when the distribution of the dispersed phase sizes is broad and only a small number of the large dispersed phases exists - an extensive quantitative evaluation may be required to obtain high accuracy.

2.3.3 The Effect of Carbon Black Dispersion

Many large black agglomerates appear when a very short mixing times are used. These large agglomerates are responsible for the poor ultimate properties, for high Mooney viscosity and for high vulcanizate modulus at low strain. As mixing proceeds, however, the large agglomerates virtually disappear but changes continue to take place in the matrix. Small agglomerates are gradually dispersed and the matrix assumes a smoother appearance. During the later stages of mixing, there is a sharp change in electrical conductivity, and a decrease in heat buildup. These changes are

related to the disappearance of the small agglomerates and the separation of the aggregates from each other.

The study of mixing rubbers and carbon black has been extensively undertaken by various groups [Tovmasyan (1983), (1989)], the number of agglomerates greater than a certain size [Nishio and Kitadono (1989)], the fraction of agglomerates [Suetsugu (1989), Yabuta and Sakaki (1990), Nakao et al. (1992), Suetsugu (1990), Tovmasyan et al. (1983, 1989), Nishio and Kitadono (1989), Svehlova and Poloucek (1990), and Shimizu (1986)]. Generally, the mixing process can be described in terms of four phases: incorporation, distribution, dispersion, and plasticization. In the incorporation phase, the filler is encapsulated and wetted by the rubber. During distribution and dispersion, the filler aggregates are pulled apart and spread out by random patterns of flow; wetting and encapsulation continue to take place on a fine scale. During the "plasticization" phase, the rubber may be extended further by the addition of oil. Flocculation of filler aggregates into soft agglomerates or network structures may occur during the later stages of mixing.

Based on the available mixing mechanisms, the dispersion of carbon black may be broadly classified into three categories: agglomeration, networking, and heterodistribution of black [Manas-Zloczower et al. (1982)]. The third type of dispersion pertains to rubber blends. Carbon black may incorporate preferentially into one rubber phase, depending on differences in saturation and viscosity of the various rubbers [Shiga (1982)].

Generally, carbon black agglomeration is the most negative aspect of dispersion. The agglomerate may exit as hard, fused lumps or as packed dry powder that has not been wetted by the rubber. Networking (microdispersion) refers to the tendency for the primary aggregates of carbon black to form a three- dimensional meshlike configuration [Nakajima

(1984)]: the smaller the particle size of the black and the higher its loading are, the more extensive the network will be. Other aspects of networking include the occlusion of rubber between the aggregates in the network and the amount of rubber-filler linkages in conjunction with the filler-filler contacts [Manas-Zloczower (1989)].

Many techniques have been developed for the subjective and direct evaluation of dispersion of carbon black [Manas-Zloczower et al. (1982), Shiga (1982), and Manas-Zloczower et al. (1989)]. They may be broadly classified into two categories: the direct visual or optical analysis, and the measurement of a particular rubber property that is closely related to dispersion [Manas-Zloczower et al. (1982)].

This study compares how various carbon black grades mix within polypropylene. Two grades of carbon black were used, having different DBPA values but the same particle size. The dispersion of carbon black in polypropylene is investigated in terms of degree of dispersion, e.g. size distribution of carbon black agglomerates at different mixing times. The goal of this work is to correlate the dispersibility of carbon black with aggregate structure i.e. high structure carbon black, low structure carbon black, and a combination of high and low structure carbon black.