CHAPTER II

THEORY

2.1 Polyethylene

Polyethylene is a commodity plastic with large consumption and great versatility. Its applications include packaging, film-sheet for agricultural purpose, toys, housewares, wire and cable covering, bottles, containers, pipes and fitting. Other applications which require high heat resistance and strength may use crosslinked polyethylene (XLPE). Polyethylene is very inert chemically, it does not dissolve in many solvents. Polyethylene has good resistance to acids and alkalis. However, it may swell slightly when it is exposed to benzene or carbontetrachloride at high temperature.

Currently, there are three kinds of polyethylene, namely the low density polyethylene, linear low density polyethylene and high density polyethylene. In the same aspect, there are derived from ethylene monomers, however, each has a different structure that bring about different properties. The property and the structures of polyethylene are shown in Table 2.1 and Figure 2.1 respectively.

2.1.1 Low Density (Branched) Polyethylene: (LDPE)

The first commercial ethylene polymer was long branched-polyethylene. Polymerization was performed at high pressure between 1,000-3,000 atm (15,000-45,000 psi) and the polymerization temperature is as high as 250° C.

2.1.2 Linear Low Density Polyethylene: (LLDPE)

Linear low density polyethylene has short chain branching. It is produced by random copolymerization with minor amounts (8-10%) of one or more alpha-olefins (vinyl monomer) such as 1-butene, 1-hexane, 1-octene, and 4-methyl-1-pentene. Polymerization are carried out at low pressure, which is similar to that for HDPE. The extended chains could be made by adding more comonomer for producing very low-density polyethylene (VLDPE) or ultralow-density polyethylene (ULDPE) which their density is less than 0.915 g/cm^3. The LLDPE's form stronger and tougher films than those from LDPE's of equivalent density.

2.1.3 High Density (Linear) Polyethylene: (HDPE)

Linear polyethylene was produced by low pressure process with the pressure of about 100 psi. The polymerization temperature is about 50 to 75 °C. Commercially, the coordinate polymerization was utilized by using catalyst an alluminium alkyl and $TiCl_4$ catalyst in a solvent such as heptane. The HDPE formed is white powder. It is insoluble in several solvents. The slurry was filtered, centrifuged, washed and dried. The

linear polyethylene has enhanced properties superior to the branched structure as shown in Table 2.1.

Table 2.1: The properties of polyethylene.

| Commercial product	Low density	Linear low density	High density
Density range, g/cm^3	0.910-0.925	0.918-0.935	0.941-0.965
Approximate % crystallinity	42-53	54-63	65-90
Branching, equivalent CH$_3$ groups/1000 carbon atoms	15-30	5-15	1-5
Crystalline melting point, °C	110-120	120-130	130-136
Hardness, Shore D	41-46	50-56	60-70
Tensile modulus, psi	0.14-0.38 x 10^5	0.38-0.75 x 10^5	0.6-1.8 x 10^5
Tensile strength, psi	600-2300	1900-4000	3100-5500
Flexural modulus, psi	0.08-0.6 x 10^5	0.6-1.15 x 10^5	1.0-206 x 10^5
Elongation (%)	90-800	100-950	200-1000
Impact strength (ft-lb/in of notch)	>16	1.0-9.0	0.5-2.0
Heat-deflection temp (°C, 264 psi)	38-49	-	60-88
Water absorption (24 hr, %)	<0.015	-	<0.01
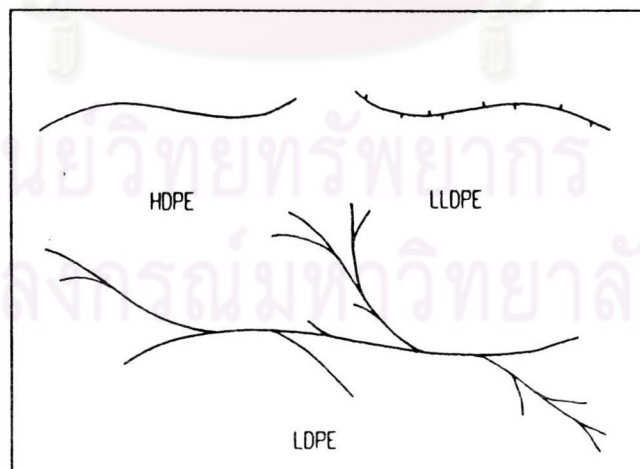
Figure 2.1: The sketch of molecular chains of low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE).

The degree of crystallinity of polymers depends on the rate of cooling during solidification and the chain configuration. The crystallinity greatly effects the density and the mechanical properties of polymers. The density of a crystalline polymer will be greater than that of the amorphous one for polymer of the same material and molecular weight. For linear polymers, crystallization is easily achieved because there are virtually no restrictions to prevent chain alignment. Any side branches interfere with crystallization, such that branched polymers are never highly crystalline. In fact, excessive branching may prevent any crystallization.

Other molecular chain characteristics, such as molecular weight, may influence the mechanical behaviors. The mechanical strength increases with molecular weight. An example of, the physical state of polyethylene as a function of the percent crystallinity, density and molecular weight is illustrated in Figure 2.2.
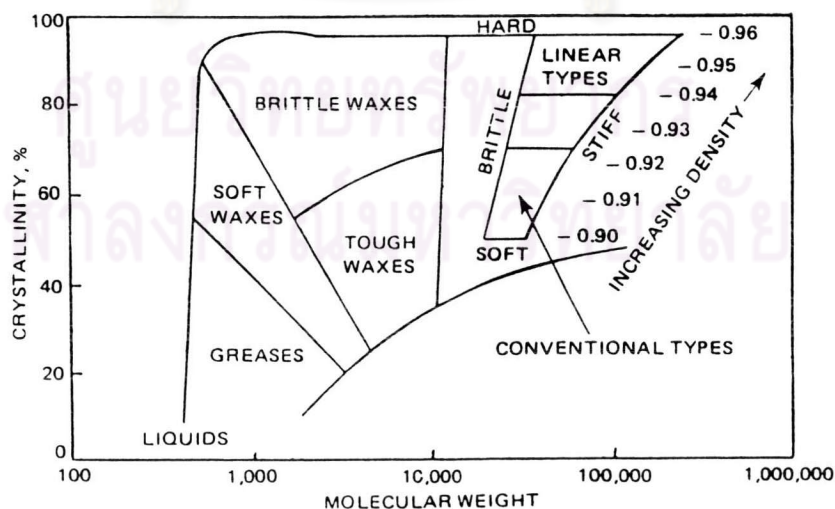
Figure 2.2: The relationship between crystallinity and molecular weight for polyethylene.

2.1.4 High and Ultrahigh Molecular Weight Polyethylene

In general, linear polyethylene has a weight averaged molecular weight (M_w) in the range of 100,000-200,000. However, the other types of polyethylene consist of higher molecular weight, these are the high molecular weight polyethylene (HMWPE) and the ultrahigh molecular weight polyethylene (UHMWPE). Commercially they are used extensively.

High Molecular Weight Polyethylene (HMWPE)

The HMWPE has a M_w in the range of 300,000-500,000. The processing conditions of HMWPE are the same as those for processing linear-polyethylene. They have improved environmental stress-cracking resistance, impact and tensile strength. HMWPE finds applications in the area of pipes, films and large blow molding containers.

Ultrahigh Molecular Weight Polyethylene (UHMWPE)

UHMWPE has a M_w in the range of 3,000,000-6,000,000. Its extraordinary properties, when compared with those of the normal polyethylene, are high abrasion and impact resistance. With their low coefficient of friction, they are used for bearing, sprockets, gaskets, valve seats, conveyor-belt parts, and other high wear resistance application. In processing, UHMWPE could not melt or flow at the normal condition of polyethylene. UHMWPE is processed mainly by compression sintering and ram extrusion into sheet and rod. Recently, the gel spinning of

UHMWPE into filaments have resulted in fibers with high tensile strength and low density.

2.1.5 Crosslinked Polyethylene: (XLPE)

Polyethylene can be converted to form crosslinked structure. It is an interesting material due to its low cost and ease of processing. A large number of properties can be improved such as the heat deformation, abrasion resistance, chemical resistance and stress cracking resistance. The impact and the tensile strengths are increased [14]. Mold shrinkage of polyethylene is decreased. And low temperature properties are improved. The applications of XLPE are focusing on cable and pipe production. The technique of crosslinking can be performed on all grades of polyethylene by radiation, peroxide and silane crosslinking technique.

2.2 Polymer Additives

Additives are substances incorporated into an organic polymers to improve their basic mechanical, physical and chemical properties. The additives are available in a broad range of functions. Some additives may be used for more than one function. For example, plasticizers are added to enhance the flexibility of the finished product but they tend to also reduce the polymer melt viscosity during processing.

The additives may be completely miscible or immiscible with the organic polymer. Generally fillers and reinforcements are immiscible. Some additives, e.g. antioxidants or ultraviolet, are usually applied at very

low concentration, while fillers or fibers are added at high concentration upto 50 % by weight. The applications of additives for polymers are illustrated in Table 2.2.

Table 2.2: Additives for polymers.

Polymer type	Anti-oxidant	Blowing agents	Flame retardant	Impact modifier	Plasticizer	UV stabilizer
Thermoplastic						
ABS	•	•		•		•
Acetal	•	•	•			
Acrylic	•	•	•	•	•	•
Cellulosics	•		•		•	•
Nylons (polyamide)	•	•	•			
Polycarbonate		•	•	•		
Polyester		•			•	•
Polyethylene	•	•	•	•		•
Polypropylene	•	•				•
Poly(phenylene oxide)		•				
Polystyrene	•	•	•		•	•
Poly(vinyl acetate)			•		•	
Poly(vinyl chloride)	•	•	•	•	•	•
Thermosetting						
Epoxy	•		•	•	•	•
Phenolic			•		•	
Polyester	•	•	•	•	•	•
Polyurethane	•	•	•	•	•	•

2.3 Polymer Composites

Polymer composites are multiple-phased materials. They are produced by adding one or more dispersing phase such as a filler or reinforcing fiber into the continuous polymer matrix. Composite systems may use different kinds and shapes of fibers or particle fillers. Possible arrangements are shown in Figure 2.3.
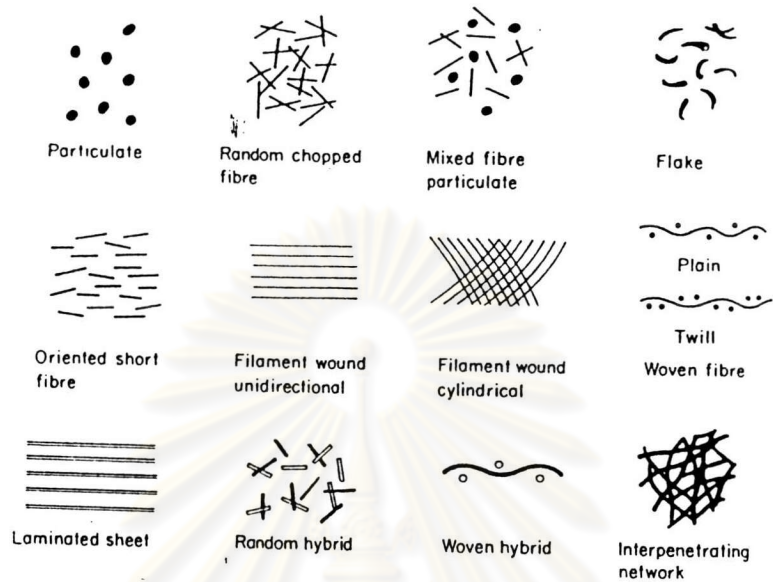
Figure 2.3: Different geometry of additives.

2.4 Fillers

Particle fillers are inert materials. They are used mainly to reduce cost and to improve strength. In thermosetting polymers, the filler is used to reduce shrinkage during crosslinking reaction. Metallic fillers are also used in plastics to increase conductivity and heat transfer. Reduction of electrostatic charging are results of the addition of graphite, carbon black, alluminium flake or metal-coated fibers.

Inorganic fillers often used for thermoplastic polymers are calcium carbonate, silicates (kaolin, talc or mica), silicas (diatomite, silica gel and alumina trihydrate) and barium sulfate (barite). They are produced most commonly by quarrying, crushing, milling, and sizing. However, some are synthesized to more uniform and finer particle size. Being readily

available in large volume and low cost, the mineral fillers are utilized extensively in large quantity in the plastics and composite industries.

Organic fillers are also used in plastics. Carbon black is used as primary filler in rubber. Wood flour is most wildely used with phenol-formaldehyde and urea-formaldehyde polymers for composite boards. Cellulose is commonly used with melamine-formaldehyde for light-colored dinnerware. Organic and inorganic fillers are indicated in Table 2.3.
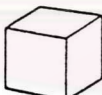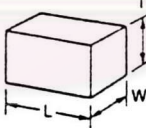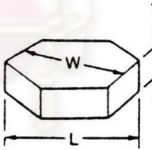
Table 2.3: The typically of fillers for polymer composites.

I. Organic Fillers	C. Metals
A. Cellulosic products	D. Boron filaments
1. Wood	E. Glass
2. Comminuted cellulose	1. Solid and hallow glass spheres
3. Fibers (cellulose, cotton, jute, rayon)	2. Milled fibers
B. Lignin-based	3. Flakes
C. Synthetic fibers	4. Fibrous glass
1. Polyesters	F. Metallic oxides
2. Nylon and UHMWPE	1. Ground fillers (zinc oxide, titania,
3.Aramid (Kevlar@) and Polyacrylonitrile	magnesia, alumina)
4. Polyvinyl alcohol (PVA)	2. Whiskers (alumina, magnesia, thoria,
D. Carbon	zirconia beryllia)
1. Carbon black	G. Calcium Carbonate
2. Graphite wiskers and filaments	1. Limestone
3. Ground petroleum coke	2. Chalk
II. Inorganic Fillers	3. Precipitated calcium carbonate
A. Silicates	H. Other Fillers
1. Minerals (asbestos, mica, China clay	1. Whiskers (nonoxides) (aluminium nitride,
{kaolinite}, talc)	boron carbide, silicon carbide, silicon
2. Synthetic (calcium silicate, aluminium	nitrile, tungsten carbide, beryllium
silicate)	carbide)
B. Silica-Based	2. Barium sulfate
1. Minerals (sand, quartz, diatomaceous	3. Barium ferrite
earth)	4. Potassium itanate
2. Synthetic	

2.4.1 Filler Particles

The selection of fillers are primary determined by the particle shape and particle size distribution. The general classification of fillers are based on the particle size and the surface area as presented in Table 2.4. Most commonly used fillers are minerals which come from rock or ores. The grinding of minerals does not lead to uniform fracture, hence the resultant particle shapes are generally irregular. Certain fabrication of fillers, such as glass spheroids and precipitated calcium carbonates, yields particles with more uniform shapes and sizes. The density and the particle size of some fillers are illustrated in Table 2.5.

Table 2.4: The particle characteristics of fillers.

Idealized shape class					
Particle Class Descriptor	Sphere spheroidal	Cube cubic prismatic rhombohedral	Block tabular prismatic pinacoid irregular	Flake platy flaky	Fiber acicular elongated fibrous
Aspect ratio	1	~1	up to 4	5-100	>10
Shape ratio;					
length (L)	1	~1	1.4-4	1	1
width (W)	1	~1	1	<1	<1-1/10
thickness (T)	1	~1	1-<1	¼-1/100	<1/10
Sedimentation diameter[a]	1	esd	esd	esd	esd
Surface area equivalence[b]	1	1.24	1.26-1.5	1.5-9.9	1.87-2.3
Examples	Glass spheres Microspheres Hallow glass	Calcite Feldspar	Calcite Feldspar Silica Barite Nephelite	Kaolin Mica Talc Graphite Hydrous Alumina	Wallstonite Tremolite Wood flour Glass fibers Anhydrite Fibers

[a]According to Stokes' law, esd = equivalent spherical diameter or diameter of sphere having the same volume as that of particle.
[b]Equivalent to spherical diameter of 1; an approximation of area when the particle has a volume equivalent to an esd of 1.

Table 2.5: General properties of fillers.

Filler	Chemical composition or formula	Density (g/cm³)	Tensile strength (N/mm²)	Modulus (N/mm²)	Hardness (Mohs)	Form	Particle size or medial (μm)
Naturally occurring calcium carbonate (chalk, limestone, marble)	CaCO₃	2.7			3	prismatic	1-15
Synthetically precipitated calcium carbonate	CaCO₃	2.1-2.5				prismatic	0.004-0.07
Natural silica (sand, quartz)	SiO₂	2.6-2.7			up to 7-7.5	aggregate of spherical partical	50-75
Synthetically silica (gel, precipitate)	SiO₂	2.2-2.5				spherical	2-40
Talc	MgO.SiO₂.H₂O	2.7-2.8			1.5	flake-shaped	10-60
Dolomite	CaMg(CO₃)₂	2.8-2.9			3	flake-shaped	1-15
Mica	K₂O.Al₂O₃.SiO₂.H₂O	2.6-2.8			2.5-3	flake-shaped	100-325
Kaolin	Al₂O₃.SiO₂.H₂O	2.2-2.6			2-3	flake-shaped	2-5
Wood flour		1.5				coarse grined to short fibers	up to 200
Wallastonite	CaSiO₃	2.85			4-4.5	fibrous	50-1250
Carbon black	C	1.7-1.8			1	spherical	Channel black: 20-30 nm Furnance black:
Alumina trihydrate	Al(OH)₃	2.4			2.5-3.5	flake-shaped	< 1-100
Barium sulphate	BaSO₄	4-4.5			3-3.5		> 10
Syenite					6-6.5		
Metal oxides: aluminium oxide	Al₂O₃	4			9	spherical	1-50
titanium oxide		4.26			6-7	spherical	0.3-3
Metal powder: aluminum	Al	2.55			2-3	spherical to	depends on
copper	Cu	8.95			2.5-3	granular	method
Glass fibers (E-glass)	Aluminium-containing boronsilicate glass	2.54	2000-3500	75000	5.5-6	fibrous	5-24
Glass microspheres	A or E-glass	2.5			6	spherical, solid	5-50
		0.15-0.38			5.5-6	spherical, hallow	20-160
Cellulose fibers	Sulphite cellulose or cotton cellulose	1.5				fibrous	20-25 220-650
Whiskers	Mineral single crystal, e.g.,Al₂O₃	3.97	19000	422000	2.8-9.8	needle-shaped	
Carbon fibers	92-99 % graphite (C)	1.75	2,800-3,000	240000-280000		fibrous	6.4-7
Graphite fibers	up to 99.9 % graphite	1.8	2,100-2,300	350,000-420,000			7-8
Boron fibers	Tungsten fiber+approx. 12 μm boron coating Carbon fiber +	2.65	3,100	400,000		fibrous	100
	boron coating	2.2	4,200	380,000		fibrous	
Aramid fibers	Poly (p-phenylene tetephthalamide) or Kevlar®	1.45	4,000	130,000		fibrous	12

2.4.2 Surface Properties

The surface of some mineral fillers consists of Si atoms with reactive groups. Usually, they are silanol groups (-Si-OH) which allows further surface treatment with coupling agents. The structure of the reactive groups of silica is shown in Figure 2.4. The silanol groups can form hydrogen bonding with free water and hence many particles may joined with the centre water molecule to form agglomerates.
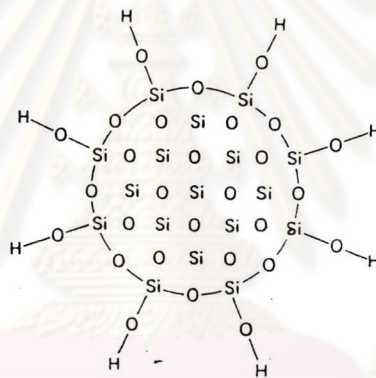

Figure 2.4: The surface structure of silica particle.

2.4.3 Hardness

Hardness is a significant property of mineral fillers. The measurement of Mohs scale is related to the abrasiveness index which reflects the ability to be scratched with a knife or a file. The hardness of mineral fillers are reported in Table 2.6.

Table 2.6: The Mohs scale of hardness for fillers.

	Value	Materials
Softest	1	talc, vermiculite 1.5
	2	fingernail
		kaolin, gypsum, tin, mica 2-2.5
		serpentine asbestos 2.0-5.0
	3	calcite, barite, copper, gold, anhydrite 3-3.5
	4	aragonite, fluorite, iron 4.5
	5	tremolite 5-6, wallastonte 5-5.5, steel knife, windowglass 5.5
	6	feldspar 6-6.5, nepheline 6-6.5, titanium dioxide pigment 6-6.5 file steel 6.5
	7	silica, zircon 7.5
	8	topaz
		corundum (alumina)
Hardest	10	diamond

2.5 Calcium Carbonate ($CaCO_3$)

Calcium carbonate is widely used as an extender or a filler. Calcium carbonate can be manufactured as fine particles with the parlicle size ranging from 0.004 to 0.07 mm by chemical precipitation. But more commonly, it is produced by crushing and subsequent fine grinding of calcite limestone rock. This latter process yields important properties such as good color characteristics and high purity. Upon heating to about 800-900°C, $CaCO_3$ decomposes, CO_2 is evolved and CaO is formed. The properties of $CaCO_3$ are shown in Table 2.7.

Table 2.7: The properties of calcium carbonate.

Properties	Calcite	Aragonite	Dolomite
Chemical composition	$CaCO_3$ most stable form	$CaCO_3$ converts to calcite	$CaCO_3$-$MgCO_3$ (45% $MgCO_3$ by wt)
Specific gravity	2.60-2.75	2.92-2.94	2.80-2.90
Hardness, Mohs	3.0	3.5-4.0	3.5-4.0
Solubility, g/100 parts water at 18°C	0.0013	0.0019	0.032
Solubility in aq. CO_2 Melting point Formation	100 time above 1339°C, 1025 atm. decomp. 900°C Limestone, marble calc-spar, chalk, eggshells, bones (with Ca phosphate) entire mountain ranges (with dolomite)	100 time above decomp. 825°C to calcite Shells of mollusks and corals; forms above 30°C; converts to calcite above 400°C and below 30°C (metastable)	100 time above decomp. 730-760°C

2.6 TALC

Talc is natural mineral of hydrated magnesium silicates with the theoretical formula of $3MgO \cdot 4SiO_2 \cdot H_2O$. It consists of 31.7 % MgO, 63.5 % SiO_4 and 4.8 % H_2O. The molecular structure of talc is oxide and hydroxide of magnesium, which are sandwiched between two sheets of silicon dioxide (silica) layer as shown in Figure 2.5. The interaction of layers are weakly bonded force. The fracture structure between this layer are often separated to form plate on flake shape.
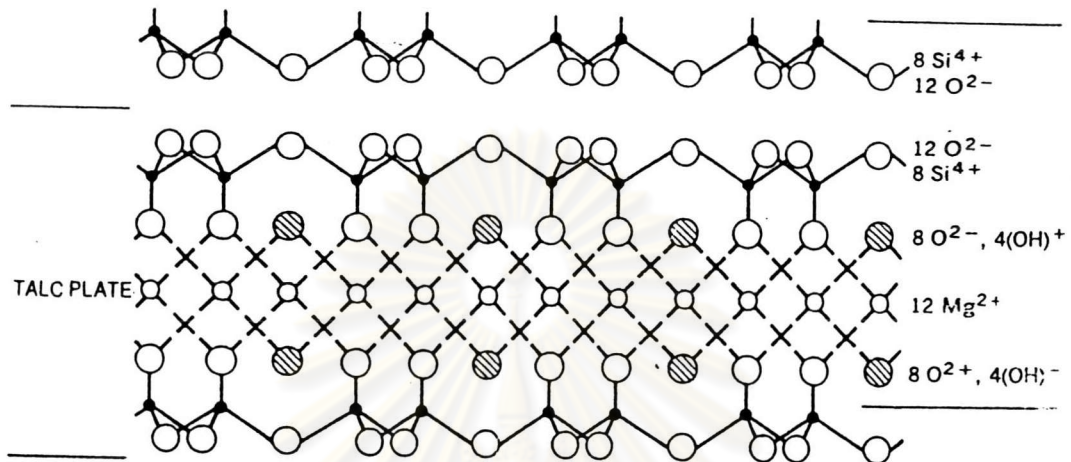
Figure 2.5: The molecular structure of talc.

The color of natural talc may be white, gray, yellow, pale blue or pale green, depending on their location and impurity. Some of the mineral contaminates associated with talc are listed in Table 2.8.

Table 2.8 : The minerals commonly found in talc deposit.

Ingredients	Chemical formula
Talc	$3MgO \cdot 4SiO_2 \cdot H_2O$
Anthophyllite	$7MgO \cdot 8SiO_2 \cdot H_2O$
Calcite	$CaCO_3$
Chlorite	$Al_2O_3 \cdot 5MgO \cdot 3SiO_2 \cdot 4H_2O$
Diopside	$CaO \cdot MgO \cdot 2SiO_2$
Dolomite	$CaCO_3 \cdot MgCO_3$
Magnesite	$MgCO_3$
Quartz	SiO_2
Serpentine	$3MgO \cdot 2SiO_2 \cdot 2H_2O$
Termolite	$2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$

2.7 Carbon Black

Carbon black are usually desired for coloring a wide range of thermoplastic and thermosetting. The enhanced properties of the finished product are improved electrical conductivity, thermal protection and effective stability under UV radiation. Applications of carbon black can be found in computer tapes, pipes, wire and cable insulation, containers and fittings. A small amount of carbon black by about 2-3 % can increase the service life time of polymers by upto 20 year or more for the outdoor products. The particle size and the number of surface active function on carbon black particles are dependent on the conditions and the manufacturing process. The functional groups on the surface of carbon black are shown in Figure 2.6.

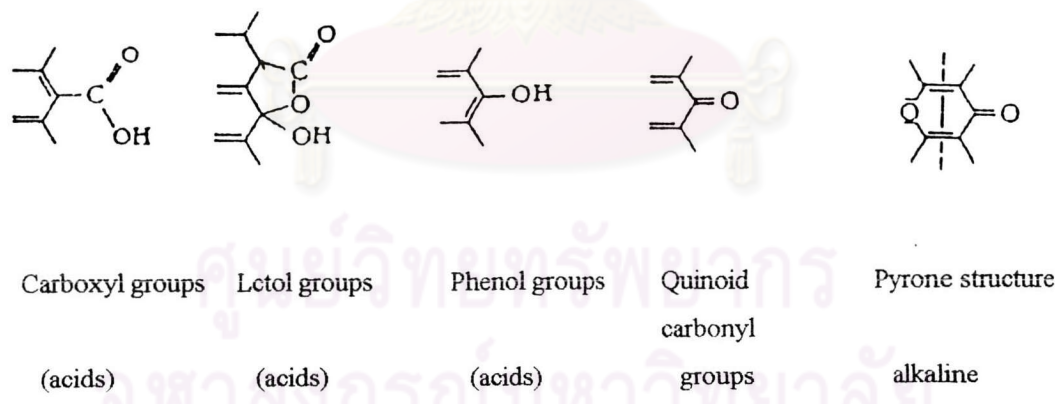| Carboxyl groups | Lctol groups | Phenol groups | Quinoid carbonyl groups | Pyrone structure |
| (acids) | (acids) | (acids) | | alkaline |

Figure 2.6: The active functional groups on carbon black surface.

Carbon black can be produced by incomplete combustion of natural and artificial gases or liquid hydrocarbons. Carbon black can be manufactured by many processes such as furnace black, channel black,

thermal black, lampblack and acetylene black process. The furnace process is commonly suitable for worldwide production.

Furnace Black Process

Highly aromatics oil feedstock is injected into the heated combustion of gas or oil flame. The feed oil is vaporized and decomposited into carbon black. The reaction is stopped by cooling with water sprays. Carbon black is separated from the gas stream by filtration.

Channel Black (Impingement) Process

In this process, many small flames of natural gas alone or with oil flames are impinged on channel or rotation metal cylinders. The carbon black is supported on the metal surface. It is then scraped off and collected.

Thermal Black Process

The chamber is heated by combustion of gas or oil. Immediately, the combustion fuel is shut off and the feedstock is injected into a heated chamber. The hydrocarbon is decomposed to give carbon and hydrogen. Carbon black is then collected and the process is repeated.

Lampblack Process

Oils are burned in metal pots with natural air draft. Carbon black deposited on metal pots and collected in settling chambers.

Acetylene Black Process

The decomposition of acetylene at high temperature forms carbon black. It is an exothermic reaction.

The properties and the type of carbon black produced by the aforementioned five process are illustrated in Table 2.9.

Table 2.9: Chemical and physical properties of carbon black produced by various processes.

Properties	Furnace black	Channel (impingement) black	Thermal black	Lampblack	Acetylene black
Mean particle diam. (A°)	13-70	10-30	150-500	50-100	350-500
Surface area (N_2) (M^2/g)	20-950	100-1125	6-15	20-100	60-70
Stiff paste oil absorption (cc/g)	0.65-2.0	1.0-5.7	0.3-0.5	1.0-1.7	3.0-3.5
pH	3.0-9.5	3.0-6.0	7.0-8.0	3.0-7.0	5.0-7.0
% Volatiles	0.3-4.0	3.0-17.0	0.1-0.5	0.3-10.0	0.3-0.4

2.8 Coupling Agents

Coupling agents are applied to enhance the molecular bonding at the interface between inorganic or organic fillers and polymer matrix. The improved adhesion at the interface is believed to increase properties such as modulus of elasticity, tensile strength, abrasive resistance and

such as modulus of elasticity, tensile strength, abrasive resistance and compression set. The two types of commercially available coupling agents are silane and titanate coupling agents.

2.8.1 Silane Coupling Agents

Silane coupling agents have a general formula as $R-Si-X_3$. In this molecule, R is an organofunctional and X is an alkoxyl group ($-OCH_3$) which can be hydrolyzed to react with the -OH bonding on inorganic surface. In use, the silane coupling agent must first be converted to reactive silanol group by hydrolysis with alcohol before reacting with reactive inorganic surface. The mechanism of the surface treatment by silane coupling agents is shown in Figure 2.7.
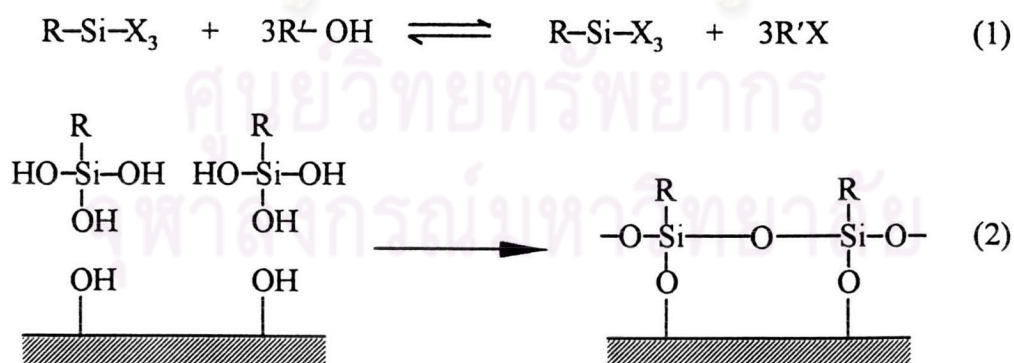
$$R-Si-X_3 \ + \ 3R'-OH \ \rightleftharpoons \ R-Si-X_3 \ + \ 3R'X \qquad (1)$$

$$(2)$$

Figure 2.7: The reaction of silane coupling agents on inorganic fillers surface.

2.8.2 Titanate Coupling Agents

Titanate coupling agents are specially designed molecule. Which are more complicated than those of the silane coupling agents. The general chemical formula is $(R-O)_m-Ti-(O-X-R^2-Y)_n$. They can be formed as monomolecular layers on most materials such as metals, metal-oxides, carbonates, sulfates, chromates, silineous materials, carbon black, graphite, Kevlar@, dispersed dyes, organic pigments and so on.

The R-O group can be hydrolyzed to react with free proton (-H) on the inorganic/organic surface. The free proton often comes from either free water or reactive portion on the fillers. The free water is present in chemical bonding and physically bonding by absorbtion on filler surface. The reaction of titanate coupling agents forms monolayer on inorganic surface as shown in Figure 2.8.
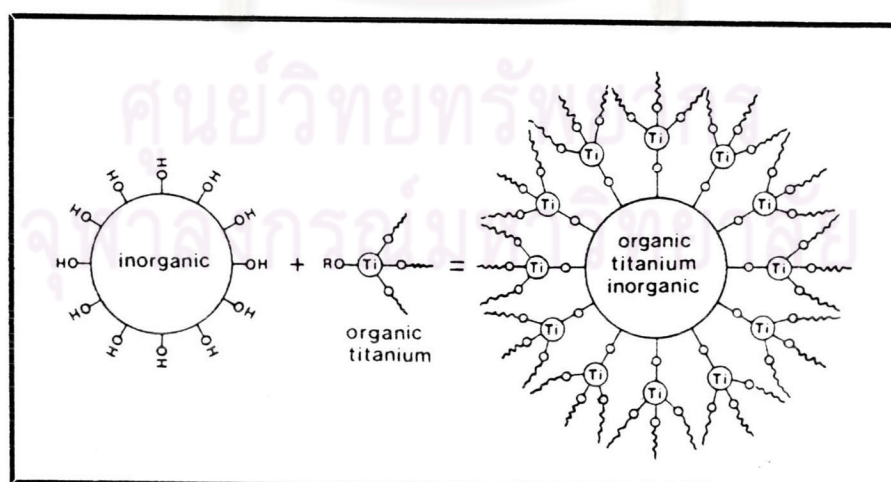
Figure 2.8: The reaction of titanate coupling agents on an inorganic filler surface.

The hydrolysis reaction occurs at room temperature (25°C) but an accelerated rate of reaction is achieved at temperature between 60-80 °C.

The X group in the titanate coupling agent chemical formula may be alkylate, carboxyl, sulfonyl, phosphate, pyrophosphate or phosphite group. It improves properties such as corrosive protection, acids resistance, antioxidant or flame retardant.

The R^2 group are aliphatic or aromatic group. They enhances the compatibility between thermoplastic and mineral fillers by promoting secondary bonding of Van der Waal's type.

The function of the Y group is to bond with thermosetting such as amino, acrylic mercapto and hydroxyl group.

2.8.3 Method of for titanate coupling agents application

The methods of surface treatment are very important for fiber reinforcement or fillers. Proper application will provide uniform distribution of small amount (<1% based on filler by weight) of liquid titanate coupling agents on the large filler surface area. The general methods of application are dry blending, slurry blending and in-situ surface treatment.

Dry blending surface treatment

The filler is placed in a mixing chamber of ribbon blender or high speed mixer. The liquid titanate coupling agent is added to a solvent to increase its volume. The coupling agent solution is fed to the filler by spray gun and mixed thoroughly until all of solvent evaporates.

Slurry blending surface treatment

The liquid titanate coupling agent is dissolved in a large quantity of solvent. It is then poured into the mixing chamber equipped with a stirrer. The filler is added while continuously stirring for complete reaction. The slurry is dried in an oven until all solvent has evaporated.

In-Situ surface treatment

All materials such as the titanate coupling agent, the polymer and the filler are pre-blended in a high speed mixer. Pre-blending is done when all materials are uniformly dispersed. Then, the pre-blend is directly used for compounding.

2.9 Factorial Designs

2.9.1 Principles

In general, factorial design is most useful and effective for experiments in which several variables are to be studied and several experimental runs are required. One can design the conditioning frame for each experiment. Factorial design generally involves the study of two or more factors at two or several levels of each variable factor. For example, if there are "a" levels of factor A and "b" levels of factor B, then each replicate contains all ab treatment combinations as shown in Table 2.10.

Table 2.10: A factorial experiment without interaction.

Factor A	Factor B	
	b_1	b_2
a_1	20	30
a_2	40	52

The effect of a factor is defined to be a change in the response produced by a change in the level of the factor. This is frequently called the main effect because it refers to the primary factors of interest in the experiment. For the data shown in Table 2.10. The main effect of factor A can be estimated as the difference between the average response at the

first level of A and the average response at the second level of A. Numerically, the main effect is as shown in Equation (2.1)

$$A = (40+52)/2 - (20+30)/2 = 21 \qquad (2.1)$$

That is, increasing factor A from level a_1 to level a_2 results in the average response increase by 21 units. Similarly, the main effect B can be estimated as shown in Equation (2.2)

$$B = (30+52)/2 - (20+40)/2 = 11 \qquad (2.2)$$

For some experiments, the difference in the response between the level of one factor may be not the same as any level of the other factors. When this occurs, there is an interaction between the factors. For examples, for the data shown in Table 2.11, at the first level of factor B, the effect A is:-

$$A = 50 - 20 = 30 \qquad (2.3)$$

and at the second level of factor B, the effect A is:-

$$A = 12 - 40 = -28 \qquad (2.4)$$

Since the effect of A depends on the level chosen for factor B, it is clear that there is an interaction between A and B.

Table 2.11: A factorial experiment with interaction.

	Factor B	
Factor A	b_1	b_2
a_1	20	40
a_2	50	12

The idea of factorial experiment is illustrated in Figure 2.9 (a) which is a plot of the response data in Table 1 against factor A for both level of factor B. The b_1 and b_2 lines are approximately parallel, this indicates a lack of interaction between factors A and B. Similarly, Figure 2.9 (b) is a plot of the response data in Table 2.11. The b_1 and b_2 line are not parallel. This indicates that there is an interaction between factors A and B.

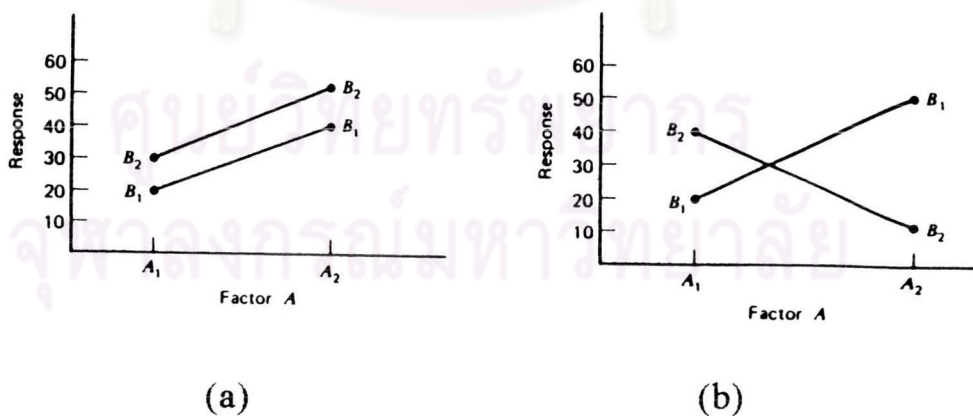(a)   (b)

Figure 2.9: Factorial experiment response and factors for (a) without interaction and (b) with interaction

When the interaction is large and the main effect is little such as the data shown in Table 2.11, the main effect A can be estimated as following:-

$$A = (50+12)/2 - (20+40)/2 = 1 \qquad (2.5)$$

As is apparent in Equation (2.5) there is no effect due to A.

2.9.2 Advantages

The advantages of the factorial design can be easily illustrated. As aforementioned, there are two factors A and B, each at two levels. The levels of the each factor are a_1, a_2, b_1, and b_1. Information on both factors could be obtained by varying the factors one at a time (simple experimental design), as shown in Table 2.12. The effect of changing the factor A is given by $a_2b_2 - a_1b_1$. If an experimental error is present, it is desirable to make two or more observations at each treatment combination and estimate the effects of the factors using average responses. Thus, a total of six observations are required in the experiment.

Table 2.12: One-factor at a time method.

Factor B

Factor A	b_1	b_2
a_1	a_1b_1	a_1b_2
a_2	a_2b_1	

If a factorial experiment had been performed, only treatment combination, a_2b_2, would have been taken. If there are four observations, two estimates of the A effect can be made as $a_2b_2 - a_1b_1$ and $a_2b_2 - a_1b_2$. Similarly, two estimates of the B effect can be made. These two estimates of each of the main effect could be averaged to produce the average main effects that are similar as those from a single-factor experiment, but only four total observations are required. The relative efficiency of the factorial design to the one-factor-at-a-time experiment is 6/4 = 1.5. Generally, it is possible to conclude that this relative efficiency of factorial design will increase as the number of factors increases, as shown in Figure 2.10.
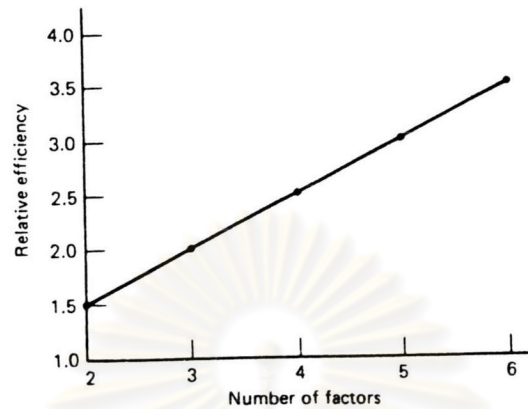
Figure 2.10: Relative efficiency of a factorial design to a one-factor-at-a-time experiment (two-factor-levels).

There is also the effect of the interaction which may be present. If the one-factor-at-a-time design indicated that a_1b_2 and a_2b_1 gave better responses than a_1b_1, the logical conclusion would be that a_2b_2 would be even better. However, if an interaction is present, this conclusion may seriously be in error. An example of which is shown in Table 2.12.

In summary, the factorial designs have several advantages. They are more efficient than one-factor-at-a-time experiments. Furthermore, a factorial design is necessary when interactions may be present and have to be taken into account to avoid misleading conclusions. Factorial designs also allow the effects of each factor to be estimated at several levels of the others, yielding conclusions that are valid over a range of experimental conditions.

2.9.3 The 2^k Factorial Design

The two-level full factorial design experiment is the best method to study the main effect of variable factors and interactions between factors. The important k factors factorial design are only two levels. These levels may be quantitative, such as temperature, pressure or time or they may be qualitative, such as type of machine, operators or types of materials. The levels of factor are high and low, and the complete replicate of two levels factorial design are $2 \times 2 \times \ldots \times 2 = 2^k$ observations. Hence, it may be called 2^k factorial design.

The 2^k design provides the smallest number of runs when compared to the k factors simple experiment. This is because there are only two levels for each factor and all observations of 2^k design can be covered at any points of experiment.

To calculate the estimate effect or to compute the sum of squares for detecting the effect and the interaction, a contrast we must first be determined. This can be done by using any of the there methods shown in Appendix 1.

The estimate effect can be evaluated by using Equation (2.6) as shown below.

$$\text{Estimate effect of factor } ABC\ldots K = \frac{2}{n2^k}\left(\text{Contrast}_{ABC\ldots K}\right) \qquad (2.6)$$

The value of the estimate effect can show the significance of the effect of each factor or the interaction but the scale of the acceptation is arbitrary.

The sums of square can be estimated by using Equations (2.7) to (2.9) as following:-

$$SS_{ABC...K} = \frac{1}{n2^k}\left(\text{Contrast}_{ABC...K}\right)^2 \qquad (2.7)$$

$$SS_T = \sum_{a-1}^{2}\sum_{b-1}^{2}\sum_{c-1}^{2}...\sum_{k-1}^{2}\sum_{n-1}^{n}(Y^2_{abc...kn}) - \frac{1}{2^k(n)}\left(\sum_{a-1}^{2}\sum_{b-1}^{2}\sum_{c-1}^{2}...\sum_{k-1}^{2}\sum_{n-1}^{n}(Y_{abc...kn})\right)^2 \qquad (2.8)$$

$$SS_E = SS_T - SS_A - SS_B - SS_{AB} - SS_C - SS_{AC} - SS_{BC} - SS_{ABC} -$$
$$...-SS_{ABC...K} \qquad (2.9)$$

The mean square can be calculated from the sum square as shown in Equation (2.10).

$$MS_{ABC...K} = (SS_{ABC...K})\,/\,\text{degree of freedom} \qquad (2.10)$$

for the F distribution

$$F_{ABC...K} = (MS_{ABC...K})\,/\,MS_E \qquad (2.11)$$

2.9.4 Indication of the Significant Effect

To search for the significant effect, two methods are available namely the analysis of variance (ANOVA) if the replication (n) is more than 2 and the normal probability cumulative plot if n is more than 1. In some cases, the moderate or large number of factors of 2^k factorial design involves many observations. For example, the 2^5 factorial design requires 32 treatment combinations and 2^6 requires 64 treatment combinations, and so on. The other reasons of conducting a factorial design is that some experiments are usually limited by the number of tests in the experiment. This may be due to some limitations for example the experiment may involve the use of very expensive material, only very little amount of material is available for the test or the experiment may involve very long test time. There is only one method that requires only one single replica and yet it can give statistically-based conclusions on the effect and the interaction of the variable parameters. This method is known as the normal probability cumulative plot. The ANOVA method uses the F distribution and more than two replicates are required; i.e. n > 2.

2.9.5 Analysis of Variance for 2^k Design

The ratio of the mean sum square of the factor to the mean sum square of error, i.e. MS_A/MS_E, MS_B/MS_E, MS_{AB}/MS_E,.......,$MS_{ABC\cdots K}/MS_E$ are distributed as F distribution and shown in Table 2.13.

Where   (2-1)   = $\nu 1$ numerator degrees of freedom

$2^k(n-1) =$ $\nu 2$ denominator degree of freedom

α = 0.05   =>   5% of reject the true hypotheses significant interaction in each factor

if F_O of $ABC...K$ > $F\alpha\,(\nu 1, \nu 2)$; factor $ABC...K$ significant interaction and large F_O => large significant interaction

Table 2.13: Analysis of variance for a 2^k design.

Source of Variation	Sum of Squares	Degree of Freedom	Mean of Squares	F_0
k main effects				
A	SS_A	1	SS_A	SS_A/SS_E
B	SS_B	1	SS_B	SS_B/SS_E
.				
.				
K	SS_K	1	SS_K	SS_K/SS_E
two-factor interactions				
AB	SS_{AB}	1	SS_{AB}	SS_{AB}/SS_E
AC	SS_{AC}	1	SS_{AC}	SS_{AC}/SS_E
.				
.				
JK	SS_{JK}	1	SS_{JK}	SS_{JK}/SS_E
three-factor interactions				
ABC	SS_{ABC}	1	SS_{ABC}	SS_{ABC}/SS_E
ABD	SS_{ABD}	1	SS_{ABD}	SS_{ABD}/SS_E
.				
.				
IJK	SS_{IJK}	1	SS_{IJK}	SS_{IJK}/SS_E
.				
.				
= 1 k-factor interaction				
$ABC...K$	$SS_{ABC...K}$	1	$SS_{ABC...K}$	$SS_{ABC...K}/SS_E$
Error	SS_E	$2^k(n-1)$	$SS_E/2^k(n-1)$	
Total	SS_T	$n2^k-1$	$SS_T/(n2^k-1)$	