

CHAPTER II

THEORY



2.1 Clay and Clay Modification

2.1.1 Clay

Clay minerals are a group of hydrous layered magnesium or aluminosilicates (phyllosilicates). Each magnesium-phyllosilicate or aluminosilicate is essentially composed of two types of sheet, octahedral and tetrahedral sheet. The tetrahedral sheet is a continuous linkage of SiO_4 tetrahedrons, in which its structure is shown in figure 2.1 through sharing of three oxygen atoms with three adjacent tetrahedral that produces a sheet with a planar network in the form of a hexagonal network [15].

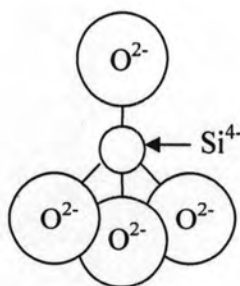


Figure 2.1: Silicon-Oxygen Tetrahedron, SiO_4 .

The another one is an octahedral sheet, which is obtained through condensation of single $\text{Mg}(\text{OH})_6^{4-}$ or $\text{Al}(\text{OH})_6^{3-}$ octahedral as shown in figure 2.2. Each oxygen atom is shared by three octahedra, but two octahedra can share only two neighboring O atoms that are arranged to form a hexagonal network [15].

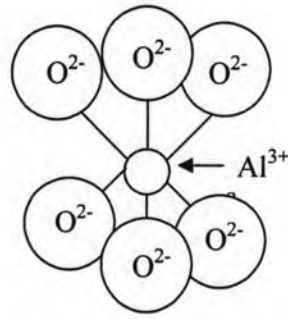


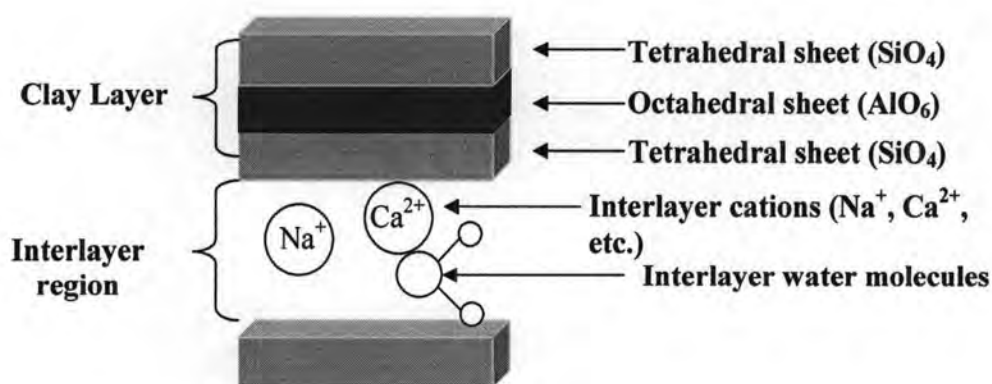
Figure 2.2: Aluminum Octahedron, $\text{Al}(\text{OH})_6^{3-}$.

The most well known layered silicate is smectite. Smectite clays or phyllosilicates have relatively weak bonding between the layers which are small flakes. Each layer consists of two sheets of silica tetrahedra with an edge-shared octahedral sheet of either alumina (aluminosilicates) or magnesia (magnesium silicates). Due to isomorphic substitution of alumina into the silicate layers (Al^{3+} for Si^{4+}) or magnesium for aluminum (Mg^{2+} for Al^{3+}), each unit cell has a negative charge between 0.5 and 1.3. The layers are held together with a layer of charge-compensating cations such as Li^+ , Na^+ , K^+ and Ca^{2+} . These charge-compensating cations provide a route to the rich intercalation chemistry and surface modification required to disperse clays at the nanoscale into polymers. The cations exchange capacity (CEC) defines the number of exchangeable interlayer cations and is usually described as meq/100 g of clay. CEC values range from 60-120 meq/100g of clay for smectite clays. There are many species of clays in a group of smectite clay minerals which consist of many layers of octahedral aluminate sheets sandwiched between tetrahedral silicate layers as list in Table 2.1. For example, montmorillonite (CEC ~76.4 - 119 meq/100g of clay) is an aluminosilicate and hectorite, which is a magnesium silicate (CEC ~ 55 meq/100g of clay) [13, 16].

Table 2.1: Species in smectite clay groups [13].

Subgroup	Species	Ideal Formula
Saponites	Saponite	$\text{Na}_{0.6}[\text{Mg}_6(\text{Al}_{0.6}\text{Si}_{7.4})\text{O}_{20}(\text{OH})_4]$
	Hectorite	$\text{Li}_{0.6}[\text{Li}_{1.6}(\text{Mg}_{4.4}\text{Si}_8)\text{O}_{20}(\text{OH})_4]$
	Fluorohectorite	$\text{Li}_{0.6}[\text{Li}_6(\text{Mg}_{4.4}\text{Si}_8)\text{O}_{20}\text{F}_4]$
Montmorillonites	Montmorillonite	$\text{Na}_{0.6}[(\text{Mg}_{0.6}\text{Al}_{3.4})\text{Si}_8\text{O}_{20}(\text{OH})_4]$
	Beidellite	$\text{Na}_{0.9}[\text{Al}_4(\text{Al}_{0.9}\text{Si}_{7.4})\text{O}_{20}(\text{OH})_4]$

Montmorillonite is one of smectite group which has a low thermal expansion coefficient and high gas barrier properties. Stacking of this structure leads to a regular weak dipolar or van der waals interaction between the layers. Isomorphic substitution in each layer generates negative charges that are counterbalanced by hydrated sodium or calcium ions residing in the interlayer spaces [13]. The general structure of montmorillonite is shown in figure 2.3.

**Figure 2.3:** Structural scheme of montmorillonite.

2.1.2 Clay Modification

Typically, the natural clay minerals are hydrophilic and the structure of clay minerals is inorganic material while the most of polymers are organic material. Therefore organically modified silicate layers can be applied in a wide range of

polymer types such as polyethylene and polypropylene. For successful formation of polymer/clay nanocomposites, alteration of clay polarity to make the clay 'organophilic' can be produced by ion exchange reactions between metallic cation of clay minerals (sodium ion) and organic cation or organic surfactant such as an alkylammonium ion. The organic cation may contain various functional groups that can interact with polymer molecules to improve adhesion strength between inorganic phase of clay minerals and the polymer matrix [13, 15]. For example, the ion exchange reaction between an inorganic metallic cation, M^{m+} , initially saturating a smectite mineral, M^{m+} -smec, and the solution of an aliphatic ammonium salt such as ethylammonium chloride, $C_2H_5NH_3Cl$, can be formulated by the following equation:



2.2 Polyamides (PA) or Nylons

Nylons are the first engineering thermoplastic and the largest family in both production volume and number of applications such as gears, rollers, shafts, impellers, bearings, films for vacuum system, cooking bags and zippers [17-18]. Originally, the name "nylon" was associated with the Dupont Company to represent the family [18]. The major producers of nylon resins have their own brand names for their polymers. Some brand names for nylon include Zytel™ (Dupont), Ultramid™ (BASF), Torayca™ (Toray), Durethan™ (Bayer), Capron™ (Allied Signal) and Akulon™ (Akzo).

Nylons can be formed by several methods in which three methods are important in commercial aspects. The first method is polycondensation of dicarboxylic acids and diamines via the salt in aqueous medium. The second method is polycondensation of ω -aminoacids. Another one is a ring opening and polymerization or polyaddition of cyclic amides e.g. caprolactam in the presence of water or in the absence of water by anionic or cationic high speed polymerization. The repeating unit of nylons is shown in figure 2.4. The subscripts a and b represent the number of methyl groups and n represents the number of repeating units in the polymer chain [17-18].

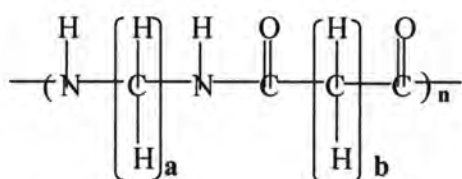


Figure 2.4: Repeating unit of nylons where subscripts a and b can be varied depending upon the type of monomers and n represents the number of repeating units in a polymer chain [17].

General family characteristics of nylons are determined by the amide group, which is presented in repeating units and is the major determiner of nylon family's properties. Both nitrogen bonds and carbonyl groups are polarity with nitrogen atom (N) and oxygen atom (O) respectively. This polarity induces the formation of secondary bonds or hydrogen bonds between adjacent nylons. These secondary bonds restrict the movement of the nylons, thus increasing their tensile strength. The secondary bonds also facilitate the close packing of nylons resulting in high crystallinity. This crystallinity leads to high strength, high stiffness, good toughness, low gas and vapor permeability, good abrasion resistance, good fatigue and high temperature processing [17].

Naturally, the polarity of the amide group makes nylons sensitive to polar solvents such as water. Water absorption of nylons is higher than most of the other engineering thermoplastics and can have a significant effect on the properties of nylons. The properties of nylons decrease with increasing the water absorption [2, 17]. Moreover, the tendency for nylons to absorb water increases significantly with increasing temperature [2, 17-18]. However, the polarity of the amide group increases the ability of nylons to be joined with traditional solvent-based adhesives many effective adhesives for nylons are commercially available [17].

For structure-dependent properties of nylons, the separation of the amide groups affects its intermolecular forces [18]. For example, cohesive forces in nylon 11 are lower than those in nylon 6 because a structure of nylon 11 is larger than that of

nylon 6. Thus nylon 11 is softer, its melting temperature and its water absorption is lower than those of nylon 6. The number of methylene groups between the amide groups also affects the melting temperature of nylon 6 [17-18]. Polymers with even number of methyl groups melt at higher temperature than those with odd number. For example, melting temperature of nylon 11 is 180 °C while nylon 12 melts at 175 °C. Moreover, viscosity of nylon increases with increasing its molecular weight [4, 11]. In addition the degree of crystallinity of nylons is also strongly affected by processing conditions [17-18]. A quenched nylon 6 can exhibit lower crystallinity than the slowly cooled nylon 6. However, adding nucleating agent into nylons can increase the rate of crystallization. The increase in crystallinity leads to greater hardness, yield stress, heat distortion temperature, abrasion resistance and modulus of elasticity compare with nylon 6 without nucleating agent. The suitable nucleating agents for nylons are silica, MoS₂, talc, iron sulfide and sodium phenyl phosphinate [18].

For the permeability to gases and vapors of nylons, the permeability to water vapor decreases in the order nylon 6, nylon 6/6, nylon 6/10, nylon 6/12, nylon 11 and nylon 12. On the other hand, the permeability to gases increases slightly in the same order. In addition, the permeability to gas and vapors is also affected by the processing method, degree of orientation and crystallinity of polymer. However, the gas permeability increases considerably with increasing moisture content and temperature [18-19].

There are several types in the family of nylons such as nylon 6, nylon 11, nylon 12, nylon 6/6, nylon 6/9 and nylon 6/10. Of these, nylon 6/6 is the most widely used of the nylon groups because of its overall balance properties such as improve heat resistance, abrasion resistance, strength and hardness. The second most widely used of nylons is nylon 6 because its properties are nearly equal to nylon 6/6 and cheaper than nylon 6/6. In addition, nylon 6 is tougher and more flexible than nylon 6/6 even at low temperature [17-18]. Therefore, nylon 6 is the alteration for production in many applications such as packaging films. The various types of nylons are shown in Table 2.2.

Table 2.2: Various types of nylons [18].

Types of nylons	Structural formula	Density (g/cm ³)	Monomers
Nylon 6	[-NH(CH ₂) ₅ CO-]	1.12 to 1.15	ε- caprolactam
Nylon 11	[-NH(CH ₂) ₁₀ CO-]	1.03 to 1.05	amino-undecanoic acid
Nylon 12	[-NH(CH ₂) ₁₁ CO-]	1.01 to 1.04	laurinlactam
Nylon 6/6	[-NH(CH ₂) ₆ NH- -CO(CH ₂) ₄ CO-]	1.13 to 1.16	hexamethylenediamine and adipinic acid
Nylon 6/9	[-NH(CH ₂) ₆ NH- -CO(CH ₂) ₇ CO-]	1.06 to 1.08	hexamethylenediamine and azelaic acid
Nylon 6/10	[-NH(CH ₂) ₆ NH- -CO(CH ₂) ₈ CO-]	1.07 to 1.09	hexamethylenediamine and sebacic acid
Nylon 6/12	[-NH(CH ₂) ₆ NH- -CO(CH ₂) ₁₀ CO-]	1.06 to 1.07	hexamethylenediamine and dodecandicarboxylic acid

Generally, nylon 6 exists in two stable crystal structures, i.e., the α -crystalline form with hydrogen bonds between antiparallel chains and the γ -crystalline form with hydrogen bonds between parallel chains. The properties of crystalline forms of nylon 6 are shown in Table 2.3. With the α -crystalline form of nylon 6, the amide and methylene groups lie within the same plane. The array of anti-parallel chains allow adjacent hydrogen bonds to produce a planar hydrogen-bonded sheet and create stacks of H-bonded sheets by repeating itself to form a monoclinic crystal, as shown in Figure 2.5 (a). For the γ -crystalline form of nylon 6, the hydrogen bonds lie between the parallel chains and the amide linkages twist approximately 60° out the plane of these molecular sheets [7], as shown in Figure 2.5 (b).

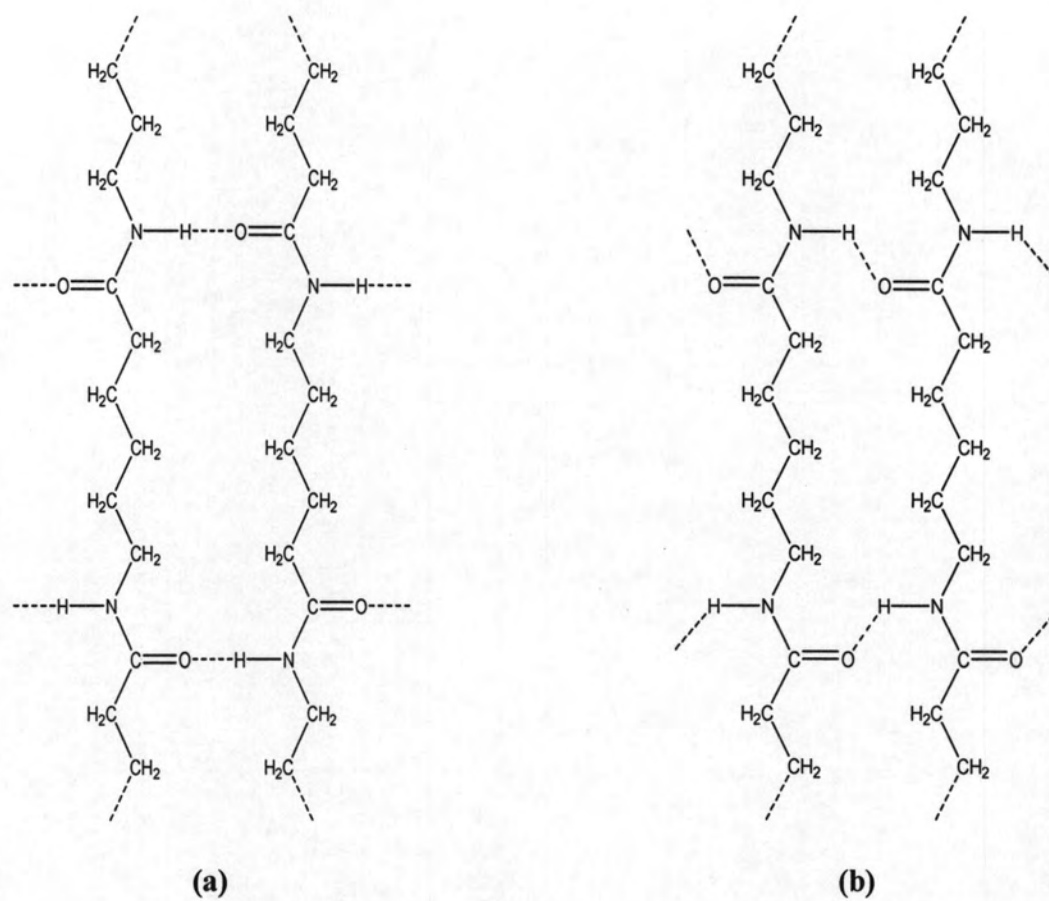


Figure 2.5: Schematic of hydrogen bonding within (a) the α -crystalline forms and (b) γ -crystalline forms of nylon 6.

Table 2.3: Miscellaneous data for the α - and γ -crystalline forms of nylon 6 [7].

Properties	α -crystalline form	γ -crystalline form
Crystal structure	Monoclinic	Hexagonal/ pseudo-hexagonal
Lattice constants	a = 0.956 nm b = 1.724 nm c = 0.801 nm $\beta = 67.5^\circ$	a = 0.472 nm ^a c = 1.688 nm ^a $\gamma = 120^\circ$ ^a
Crystallographic reflection (s)	(200) (002/202)	(001) (200/20 $\bar{1}$)
Characteristic d-spacings	d ₂₀₀ \approx 0.370 nm d ₀₀₂ and d ₂₀₂ \approx 0.440 nm	d ₀₀₁ \approx 0.413 nm
Density, ρ (g/cm ³)	1.23 (experimental) 1.23 (calculated)	1.16-1.19 (experiment) 1.16 (calculated)
Heat of fusion, ΔH°_f (J/g)	241	239

^a Hexagonal lattice constants were calculated based on the monoclinic parameters, a = 0.993 nm, b = 1.688 nm, c = 0.478 nm and $\beta = 121^\circ$. The hexagonal lattice constant, a, was taken as the average of a and half of b of the monoclinic unit cell. The constant c representing the fiber axis remained fixed.

2.3 Polymer/Clay Nanocomposites

Composite materials are formed when at least two materials are mixed. Conventional composites are called when phase mixing occurs in a macroscopic (μm) length scale while nanocomposites occur on a nanometer length scale. In addition, nanocomposites can improve several properties such as mechanical, barrier and thermal properties because of their unique phase morphology and improved interfacial properties.

2.3.1 Types of Polymer/Clay Nanocomposites

The dispersion of clay minerals in polymer matrix can be characterized in three general types of composite materials which are shown in figure 2.6 [20]. The conventional composite contains clay tactoids in aggregated state with unintercalated polymer along the silicate layers. The clay tactoids are simply dispersed as a segregated phase. The intercalated nanocomposite is formed by the insertion of one or more molecular chains of polymer between clay galleries, resulting in an expanded interlayer distance. The exfoliated nanocomposite is formed when silicate nanolayers are individually dispersed in polymer.

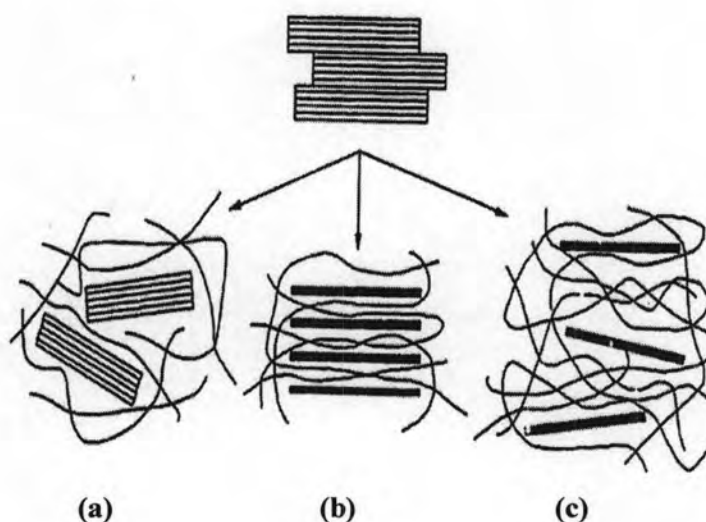


Figure 2.6: Illustration of the three possible types of polymer/clay nanocomposites: (a) Conventional composites, (b) Intercalated nanocomposite, (c) Exfoliated nanocomposite [20].

More importantly, each nanolayer in an exfoliated nanocomposite contributes fully to interfacial interactions with polymer matrix. This structural distinction is the primary reason why the exfoliated clay state is especially effective in improving the reinforcement and other performance properties of clay composite materials [13, 20].

2.3.2 Polymer/Clay Nanocomposite Preparation Methods

The polymer/clay nanocomposites may be obtained mainly by three methods which are solution method, in situ polymerization and melt processing. In the solution method, nanocomposite is formed by dissolving the soluble polymer into an organic solvent. The clay is then dispersed in the obtained solution. Therefore, this technique allows modification of the particle surface without drying, which reduces particle agglomeration problem. After that the nanoparticle/polymer solution can be cast and dried. The nanoparticle/polymer can be isolated from solution by solvent evaporation or precipitation. Unlike the solution method, nanoscale particles are dispersed in monomer and the result mixture is polymerized in an in situ polymerization methods. Thus, polymer chains are grown and push layered silicate to be apart from each other. On the other hand, melt processing method, the silicates layers are directly dispersed into the polymers while polymers are in a melted state. In order to use this method, layered silicates need to be previously surface treated through the organo-modification like previously mentioned (see in section 2.1.2). Among these techniques, melt processing method is the most attractive way because of its low cost, high productivity and compatibility with current polymer processing techniques [5, 16, 21].

2.3.3 Gas Barrier Enhancement

The excellent gas barrier properties of films are needed especially in food packaging application in order to extend its shelflife. Polymer/clay nanocomposites have attracted more attention in food packaging films because incorporation of relatively small quantities of nanoclay materials in polymer matrix can increase the pathway of gas through the films as shown in figure 2.7. Moreover, the high aspect ratio of nanoclays also contributes to overall barrier performance [22-23].

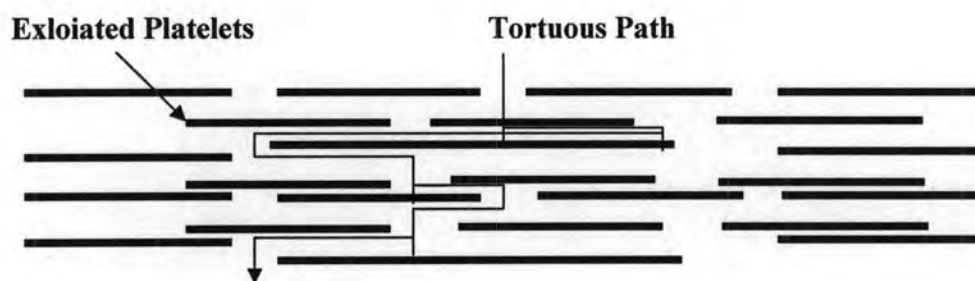


Figure 2.7: Illustration of tortuous path of gas through polymer/clay nanocomposite films [22].

2.4 Extrusion Process

Extrusion is the process where a solid plastic, usually in the form of beads or pellets, is converted into a particular form with different shape. A cold plastic material is carried by the action of the screw, which consists of three sections, and heated in order to change into the molten state. During the process, it creates a pressure on material before the molten plastic enters the die. A pressure which creates on the materials forced through into the die. The screen pack, which composes of a number of coarse mesh and is placed between the screw and the die, can help filter out dirt from polymer matrix. After that the molten plastic is extruded through the die with different shape and cooled at below melting temperature or glass transition.

Extruders which are shown in figure 2.8 have a several applications in processing of polymer such as blow molding process and blown film process which is widely used to produce films [24].

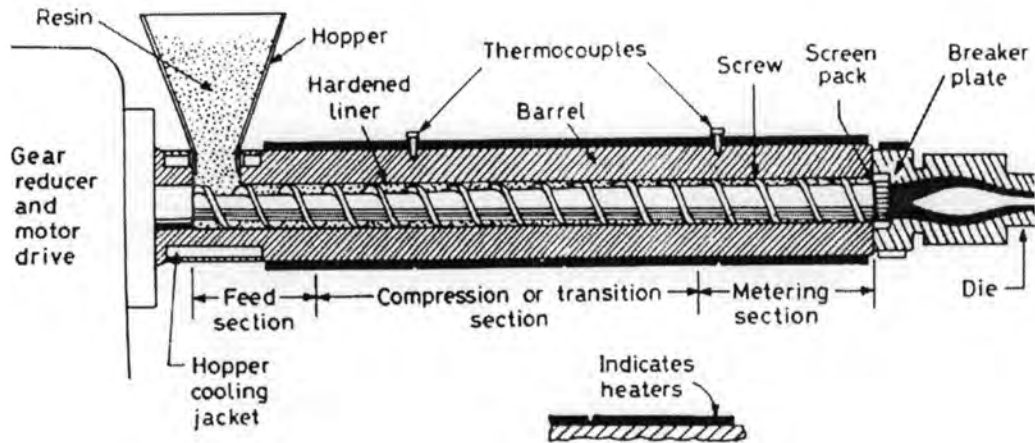


Figure 2.8: Scheme for a typical single –screw extruder [24].

2.4.1 Blown Film Extrusion

One of the most common methods in making films is blown film extrusion. At present, Blown film extrusion can be widely used for the manufacture of monolayer and multilayer films for high barrier applications such as food packaging. In addition to industrial packaging e.g. shrink film, stretch film and bag film. Blown film extrusion is shown in figure 2.9. In this figure, the molten plastic is fed through the circular die with different diameter. The bubble film is then expanded in vertical or horizontal direction by internal and external air with different blow up ratio which is defined as a ratio of bubble diameter to die diameter. After that the expanded bubble film is moved into the pinch rolls to squeeze it and formed as a flatten film.

This fabrication process has several advantages such as regulation of film width and thickness which is controlled by the speed of screw, the volume of air in the bubble and the output of the extruder. Moreover, eliminate end effects (e.g. edge bead trim and non uniform temperature) and capability of biaxial orientation, allows the uniformity of mechanical properties, are also the other advantages of blown film extrusion [24].

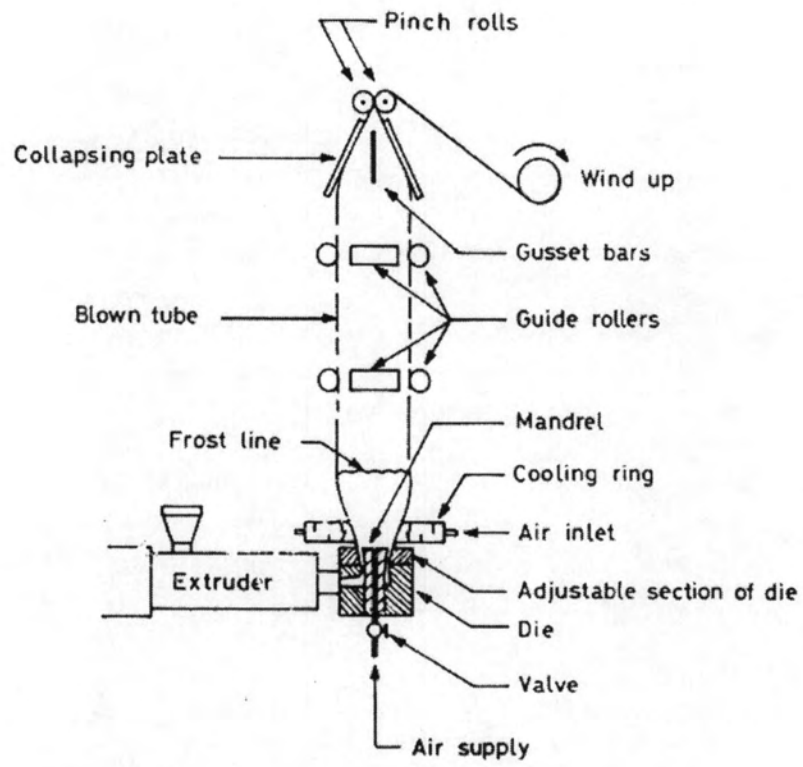


Figure 2.9: Scheme for blown-film extrusion [24].