CHAPTER II

BACKGROUND

2.1 Introduction

In order to study the relationships of structure and barrier properties, many of related knowledge must be concerned. This chapter provides the involving knowledge, beginning with transport phenomena in polymers including parameters influencing transport property, development of barrier property through polymer blending, morphological control via blending, as well as properties of materials used, i.e., LCP and PE. Models for prediction transport properties of blends are presented at the end of this chapter. Prediction of mechanical properties by composite theory is also discussed.

2.2 General Principle of Transport Phenomena in Polymeric System

Transportation of small molecules through a polymeric membrane is a process involving sorption, diffusion, and permeation. The process occurs due to random molecular motion of individual molecules, which have the concentration or pressure difference between two phases as a driving force [25,26].

In 1829, Thomas Graham first investigated the gas permeation through polymeric material [2]. It was in 1866, when Graham formulated the "solution-diffusion process", where he postulated that the permeation process involved the dissolving of the prenetrant in the upstream face of membrane, followed by diffusion to the downstream face where the gas evaporation outward occurs (illustrated in Figure 2.1). Thus, the process can be mathematically expressed as in Equation (2.1), namely solution-diffusion model.

$$P = D.S$$

Equation (2.1)

Where
P = Permeability coefficient.

D = Diffusion coefficient.

S = Solubility coefficient.

The "solution-diffusion process" mechanism still prevails today. The three transport coefficients involve with this process i.e. permeability, solubility, and diffusion coefficients are described in the three following subsections.
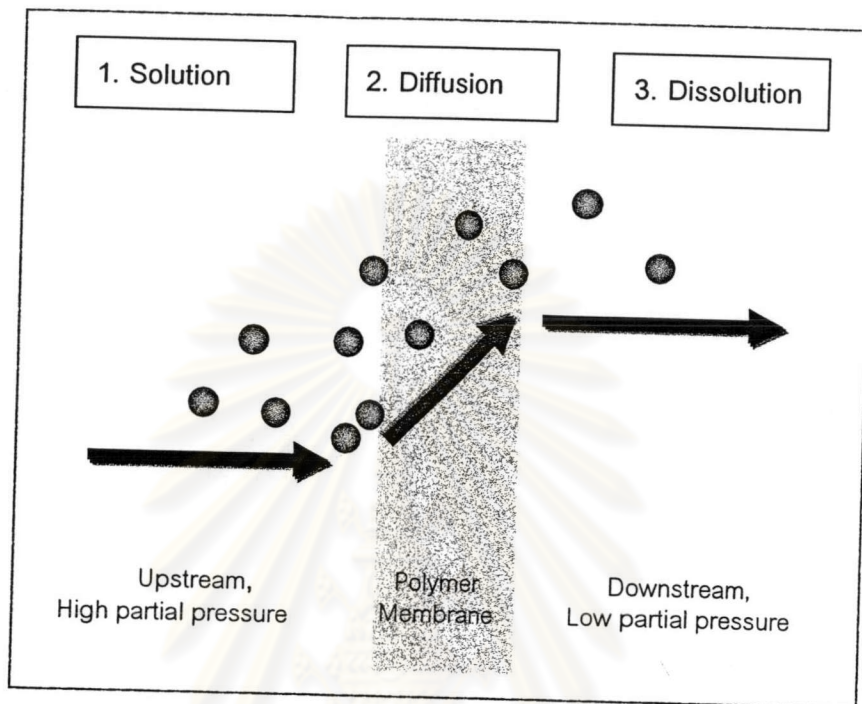

Figure 2.1 "Solution-diffusion" process

2.2.1 Solubility Coefficient (S)

The solubility coefficient (S) or sometimes referred as the sorption coefficient is a measure of the amount of gas sorbed by the membrane. S is a thermodynamics factor related to the specific interactions between the gas molecules and the polymers. S increases with the penetrant condensability, the permeant size, the polymer free volume, the free volume distribution, and polymer/gas interactions.

The solubility coefficient S is defined as

$$S = \frac{C}{P}$$

Equation (2.2)

where   C is equilibrium concentration of gas on polymer.

P is pressure of gas.

2.2.2 Diffusion Coefficient (D)

Diffusion or diffusivity coefficient (D) indicates the rate of a penetrant that transports through the membrane. It is commonly correlated with the overall free volume content. The penetrant size and shape, the polymer free volume, the segmental mobility, and the rigidity of the polymer chains affect diffusion coefficient.

Diffusion coefficient can be considered as independent of gas concentration for a simple gas, where the interactions with the polymer are weak. Diffusion coefficient follows the Arrhenius-type relationship given as

$$D = D_0 \exp\left[\frac{E_D}{RT}\right]$$ Equation (2.3)

Where D_0 is the pre exponential factor

E_D is the activation energy of diffusion

R is universal gas constant

T is absolute temperature.

Increasing of gas volume fraction and decreasing of permeant size tend to decrease E_D. However, the Equation (2.3) can apply only in non-plasticizing systems. In the case of plasticization, Henry's law will be applied.

$$D(c) = D_0 \exp(\gamma.C)$$ Equation (2.4)

Where γ is a plasticizing parameter depending on the system at

given temperature and

D_0 is the diffusion coefficient at zero concentration.

For the system which interactions between gas and polymer are strong, the Equation (2.5) is applied

$$D(c) = D_0 \exp(AB)$$ Equation (2.5)

Where   A is a temperature dependent parameter and

B depends on concentration, volume fraction or activity

2.2.3 Permeation Coefficient (P)

Permeation or permeation coefficient (P) is the amount of substance passing through a polymer membrane, involving adsorption on one surface, diffusion to the other surface and dissolution on the other side. Permeability coefficient P is the product of the diffusion and solubility coefficients, as described previously.

The permeability coefficient (P) varies differently with pressure depending on the nature of the gas and that of the polymer. The permeability of permanent gases such as H_2, He, N_2 and O_2 in rubbery or glassy polymeric membranes is not really affected by variation in pressure in a reasonable rang (typically about 10 atm). The permeability of other gases in glassy polymers decreases with pressure, while it increases in rubbery polymers. The permeability generally decreases as the permeant size increase. Moreover, the lower the density or the higher the free volume leads to the higher permeability. Cross-linking, crystallinity, and orientation decrease P.

P also increases with temperature and can be represented by Arrhenius-type relationship

$$P = P_0 exp\left[\frac{E_p}{RT}\right]$$
        Equation (2.6)

Where   P= Permeability

P_0= Permeability at infinite temperature

E_p =Activation energy of permeation.

Below the glass transition, permeability increases slowly with increasing temperature, molecules of the substrate (polymer) become increasingly mobile as temperature increases, and the permeability increases more rapidly.

Permeant behavior depends on both solubility and diffusivity. Note that either a low diffusivity or low solubility coefficient can account for a low value of permeability, or high value of either will likewise account for a high permeability.

From the general knowledge of transport phenomena in polymers, diffusivity and solubility play a key role on permeation process. The powerful factor is chemical nature of both permeate gases and polymers. The parameters derived from chemical structure i.e. polarity, inter-chain forces, and chain stiffness. In spite of this, different systems of polymers, glassy and rubbery, respond each parameter with different ways as some were described above. Moreover, in the system of crystalline polymer, which involving some order in the structure exhibits even more complex in responding.

2.3 What Effects on Permeability in the Crystalline Polymer

Reduction of permeability in semi-crystalline polymer has been taken as the advantage for barrier applications. Semi-crystalline polymer was considered as inhomogeneous materials with impermeable microcrystalline regions embedded in a continuous of an amorphous substance. Transportations of gases are assumed occurring in the amorphous region where possesses effective free volume. Chain packing in polymer crystallites precludes the diffusion and the dissolution of even small gas molecule [2]. In this system, "tortuous concept" is often applied. "Tortuosity", accordingly, is an accounting for impedance of flow offered by the increased effective path length as well as variations in the cross sectional area of the conducting region. The tortuosity is dependent upon the size, shape, and anisotropic nature of crystalline phase. Changing in crystalline phase by heating, cooling, annealing, or drawing can affect directly to tortuosity of the system. Furthermore, varying of crystallinitys also affect mobility of polymer chains in amorphous region which may lead to increase or decrease of permeability. The following sections explain about the effects of molecular order including of crystallinity and orientation on barrier properties.

2.3.1 The Effects of Crystallinity and Morphology on Barrier Properties

Crystallinity is a fraction of crystal to overall system. Effects of crystallity on the permeability are very complex. While solubility can be simply related to crystallinity, usually decreases linearly with increasing crystal fraction, diffusivity is rather

complex by involving with the details of polymer morphology. For example, lamellae structures, developed by drawing, were observed to be the effective structure, which has the higher tortuosity than that of spherulitic structures. In case of annealing of semi-crystalline polymers, it results in reduction of the tortuosity as much as 50% although large increases in crystalline size. This had been suggested to the result of the formation of permeability gap in the crystallite [2].

In addition, crystal also affects the chain immobilization in amorphous region that results further in decreasing of the permeability. The chain immobilization increase activation energy of diffusion (E_D) that observed in the amorphous phase upon crystallization.

2.3.2 The Effects of Molecular Orientation on Barrier Properties

Molecular orientations take place during or post of processing. Stretching or drawing of polymer films is used to improve mechanical behavior, and it can lead to improved barrier properties. The degree of orientation achieved is primarily dependent upon the draw ratio and processing condition. Depending on the mode of deformation, the permeability of polymer may increase or decrease.

During the film extrusion process, for instance, crystallization from an oriented melt may occur. The crystalline microstructure is highly depending upon the degree of strain imposed. Spherulitic, lamellar, and shish kebab morphologies achieved by increasing level of stress from zero or low stress to exceedingly high levels of strain imposed by the processing condition. Lamellar structure, as mention before, is preferred for barrier improving compared to spherulitic structure while shish kebab had also been reported to cause the permeability increase [2].

Post drawing, or sometime referred to cold drawing, is usually performed under melting points of polymers. Transformations of existing crystallites are taking place. The final structures strongly depend on the initial structures and the stress levels. In brief, the transformation of the spherulitic structure to a microfibrillar structure brings about marked decrease in the transport coefficient. Polyethylene at the high draw ratios gives over a hundred fold decreasing in diffusion coefficient, for example.

In addition, uniaxial and biaxial orientations also show different effects on permeability. Study on poly (ethylene terephthalate) (PET) indicated that the grater unbalanced of the biaxial orientation, resulting the more reductions in permeability. Interpretations were considered of conformation changes in polymer backbone itself. When the trans isomers are increased, the chain packing efficiency in amorphous region is improved. While, the trans isomers level of biaxial oriented films in balanced state is limited at ~55%, in uniaxial stretching, it can be increased to 89% at a draw ratio of 5.5 [2].

2.4 High Barrier Polymers

In searching for high barrier polymer, it is desirable to minimize both D and S as much as possible. The most powerful overwhelm permeability is the chemical nature of polymer. Nowadays, many high barrier polymers are available. For example

1. Cellophane: In packaging, cellophane was the first practical film [2]. It is an excellent gas barrier in the dry state; however, cellophane is sensitive to moisture [25]. Relative humidity of 50% increases the permeability of an order of magnitude and at 90% RH, this polymer is virtually removed from the class of high barriers by further increasing the permeability of more than ten-fold [1].

2. Polyvinyl chloride (PVC) and their copolymers: Polyvinyl chloride (PVC) is an economical thermoplastic film with good barrier properties to gases and water. However, processing of PVC needs some additives such as plasticizer that resulting in the vanishing of high barrier performance. Difficulty in processing of PVC leads the later developments of even higher barrier resin based on copolymers of vinylidene chloride and vinyl chloride, namely Saran$^{\circledR}$, produced many new packaging opportunities.

3. Ethylene-vinyl alcohol (EVOH) copolymers: Ethylene-vinyl alcohol copolymers (EVOH) were discovered to be excellent oxygen barriers; these polymers combine a strong hydrogen bonded amorphous phase like that of

cellophane with a partial crystalline nature. The presence of the $-OH$ group is the principle key to lower gas permeability of EVOH; the greater the number of $-OH$ groups per molecular chain, the lower the permeability. However, while these materials have incredibly low permeabilities to oxygen in dry state, like cellophane, they lose their barrier capability at high relative humidity [2].

4. **Polyamides or nylons (PA):** Polyamide family comprises a wide range of thermoplastic polymer resulting from the condensation of a monomer containing amide group with one containing an acid group. The characteristics repeating unit $-CONH-$ accounts for the mechanical strength and barrier properties of polyamides. Semi crystalline PA when dry limits the transfer of gases, however, like in EVOH, the barrier properties is diminished by moisture. In contrast, barrier properties of amorphous polyamide, known as MXD6, are improved with increasing humidity.

5. **Liquid crystalline polymers (LCPs):** LCPs, new class of polymers, are new candidates of high barrier material. The uniqueness of their structure results in unusual features such as rheological behavior, high mechanical properties, and barrier characteristics. More details of this polymer are described later in this chapter.

Some limitations, as seen in Table 2.1, prohibit utilizing high barrier polymers as a single material. Blending is the alternative way to employ the advantages of these high barrier polymers, while the limitations can be reduced or even eradicated.

Table 2.1 Principal advantages and disadvantages of some high barrier polymers [1]

Polymer	Advantages	Disadvantages
EVOH	• Very high gas barrier if dry • Stiff and strong • Clear transparent in films	• Moisture sensitive, Barrier required protection • Form jell in extrusion
PAN	• Stiff, strong • High barrier to gases, oils • High chemical resistance	• Residual monomer content may cause the health hazard
PA	• Good flavor and aroma barrier	• Properties depend on moisture content
PVC	• Tough, flexible, clear, transparent • Oil resistance • Moderate barrier	• narrow range of using temperature
PVDC	• High gas and moisture barrier • Unaffected by moisture	• Subject to thermal degradation during extrusion
LCPs	• High gas and moisture barrier • High chemical resistance • Unaffected by moisture • Stiff, strong	• Highly anisotropic properties • Hazy

2.5 Development of Barrier Materials by Blending

Blending is a well-known technique use for combining two or more polymers together. The advantages of the two polymers can be achieved without requirement of synthesis new polymer.

Development of barrier materials by blending is the new approach receiving the large amount of attention in recent years. Concept of producing high barrier film by blending is to create the tortuous path by adding high barrier polymer into the conventional one, this occurs in immiscible blend system [1-3]. As shown in Figure 2.2, the longer distance a gas has to travel, the slower of permeation rate is. In other words, tortuous paths developed in an immiscible blend film can result in the final high barrier property.
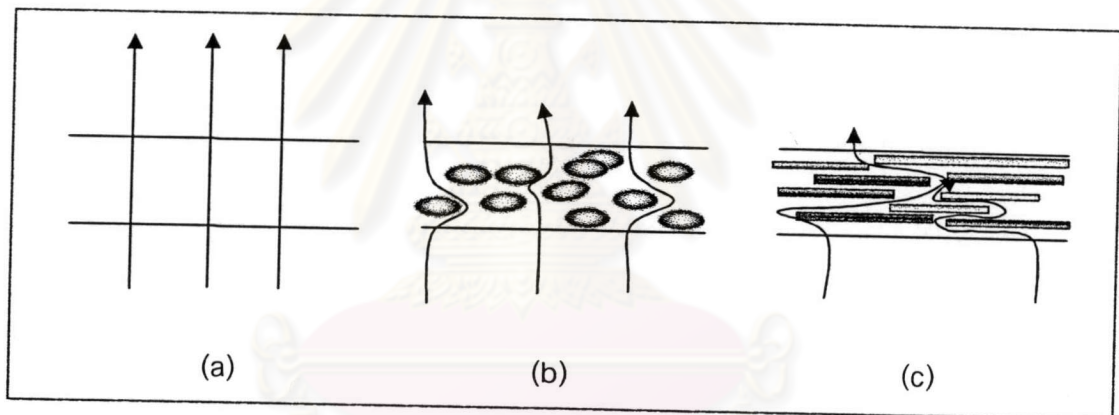

Figure 2.2 Tortuous path concept of polymer blend ; (a) single polymer, (b) polymer blend with droplet structure, and (c) polymer blend with fibrous structure (⬭ and ▬ illustrate geometry of an impermeable phase, where arrow (⟶) represents gas's path) [1]

It is clearly seen that barrier property of polymer blend film significantly depends on the final morphology of the blend including size, shape, dispersion, and distribution of a high barrier impermeable phase. Morphology is generally controlled by rheological behavior of polymer component, blend composition, processing method and conditions. Commonly, barrier property could be modestly improved when achieving droplet and fibrous structure. Barrier characteristics could also increase with increasing

content of high barrier polymer component. The highest barrier property could be obtained from laminar structure in the films. Various works have been carried out on EVOH and Nylon as was prier mentioned. However, both Nylon and EVOH sacrifice their barrier properties in humid condition. It is, therefore, proposed in this study that such a shortcoming of Nylon and EVOH can be overcome by utilizing liquid crystalline polymer (LCP), the outstanding engineering polymer with unique rheological property.

2.6 Polymer Blends Containing LCPs

Over the past two decades, Liquid crystalline polymers (LCPs) have received a considerable amount of attention in both academic and industrial laboratory. Before taking to challenge of using LCP as a high barrier, background and some properties of LCP should be addressed.

2.6.1 Liquid Crystalline Polymers (LCPs)

2.6.1.1 Liquid Crystal

The term "liquid crystal" describes a state of matter, which is an intermediate between the isotropic liquid state and the three dimensional crystal lattice. It is also referred to the term "mesophase" (Greek, mesos = intermediate). Retizner provided the first scientific description of liquid crystal in 1888 and a year after Lehman made the experiment to confirm Retizner and coined the term "liquid crystal" [27-28].

There are many different types of liquid crystal but there are three main classifications as recognized by Friedel [27], i.e. nematic, smectic, and cholesteric. The molecule organization in a nematic mesophase (from Greek nemá, thread) involves molecular alignment without a special regularity (order in one direction). For smectic (from Greek smegma, soap), the molecules are aligned and stratified, ordering in two directions. Cholesteric mesophase comprise a helical nematic or smectic structure or a rotational order. These three classes were illustrated in Figure 2.3.
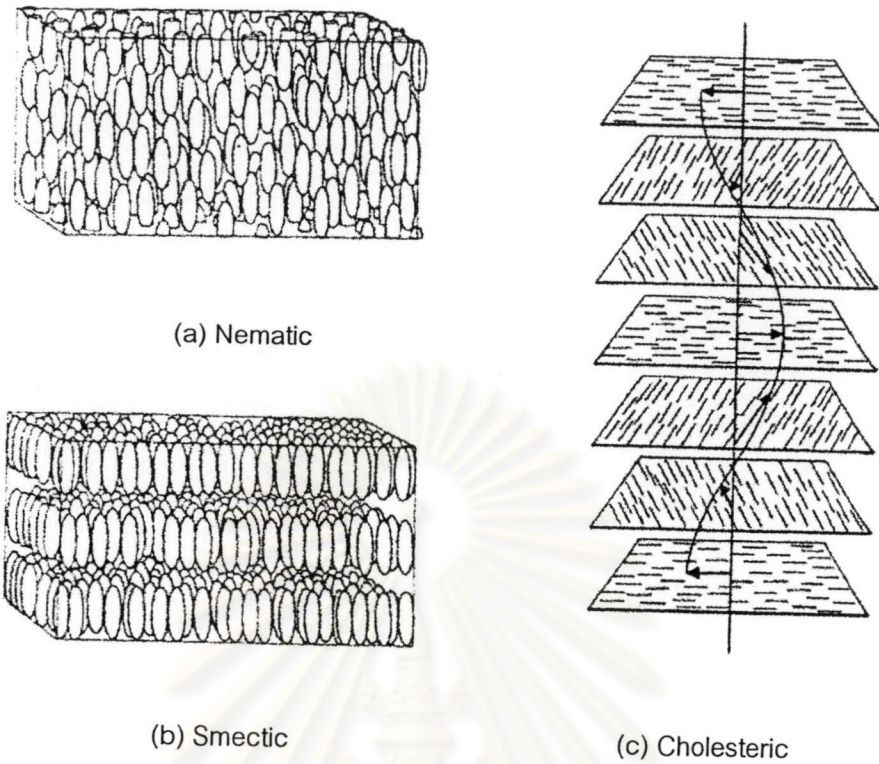
(a) Nematic

(b) Smectic

(c) Cholesteric

Figure 2.3 The Schematic diagrams of molecular arrangements of liquid crystal (a) Nematic, (b) Smectic, and (c) Cholesteric [28]

Almost any form of molecular anisotropy can give rise to liquid crystal phase (see Figure 2.4). The extending the length of these molecules by polymerization can receive the unique polymer as called Liquid Crystalline Polymers or LCPs.
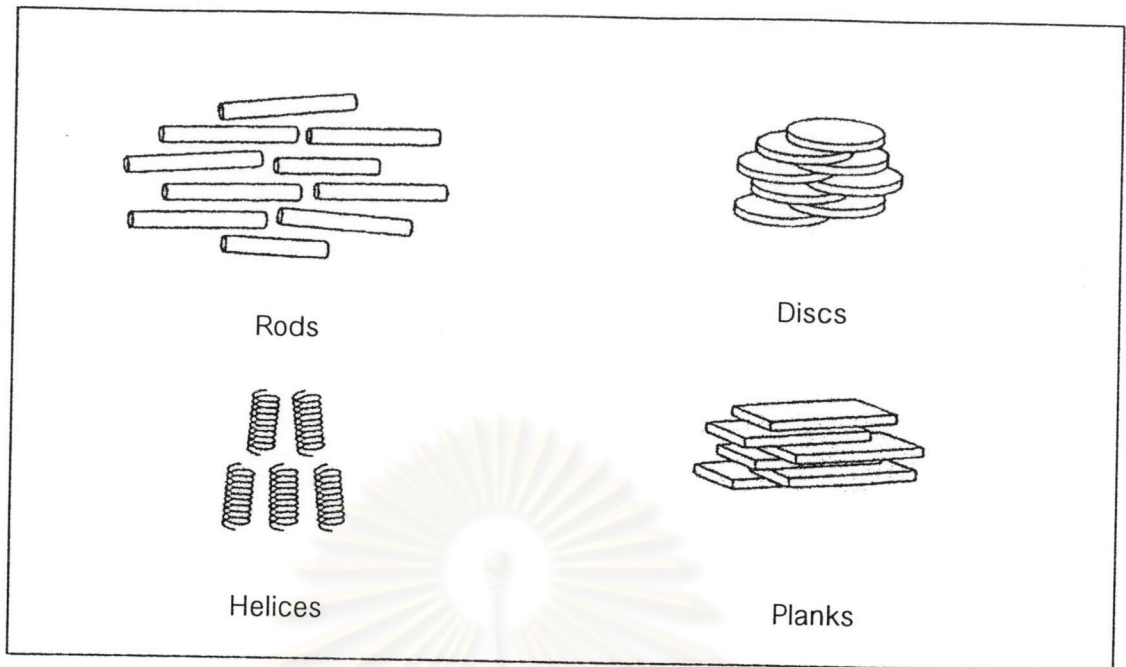
Figure 2.4 Anisotropic units giving rise to liquid phases [29]

2.6.1.2 Liquid Crystalline Polymers (LCPs)

Liquid crystalline polymers (LCPs) are polymers typically consisting of repeating mesogenic monomer units that exhibit liquid crystal behavior. The mesogenic unit, e.g. rod-like, disc-like, can be found in the main chain, in the side chain or in both (see Figure 2.5). LCPs can be classified into two-principle categories based on the intermediate state in the polymer. The phase change from crystal to liquid crystal can be achieved either by heating, in which case it is called "thermotropic" or by dissolution, in which case it is called "lyotropic". However, unlike flexible polymers that exhibit a random coil configuration in the melt or in solution, LCPs maintain a partially crystalline order even on meting as shown in Figure 2.6.
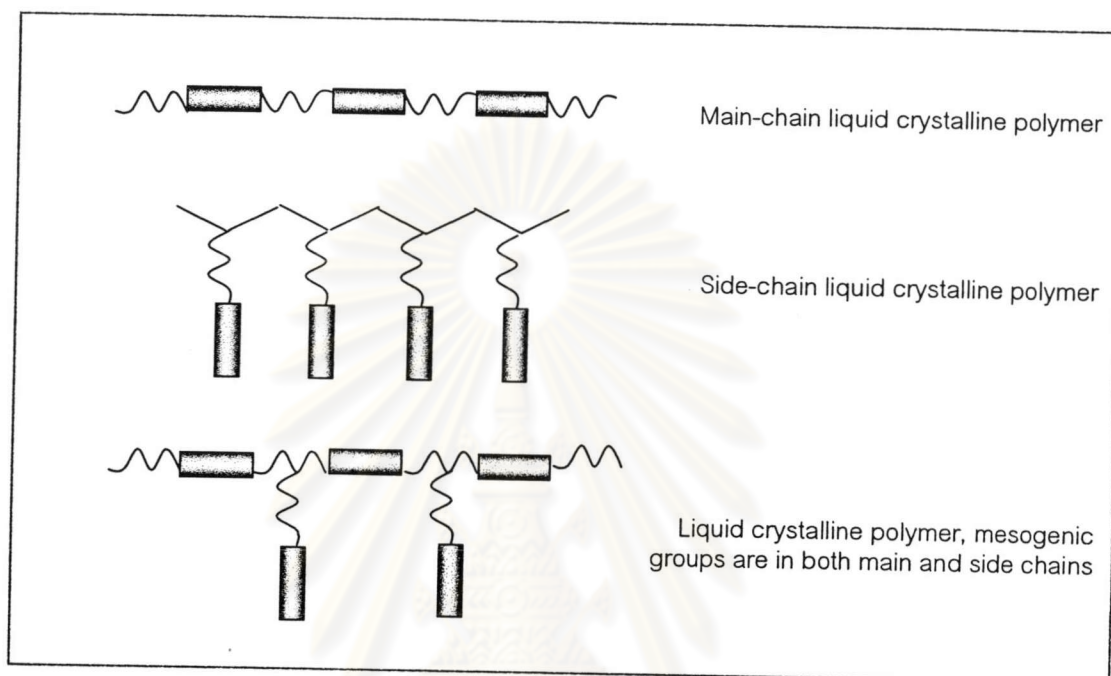
Main-chain liquid crystalline polymer

Side-chain liquid crystalline polymer

Liquid crystalline polymer, mesogenic groups are in both main and side chains

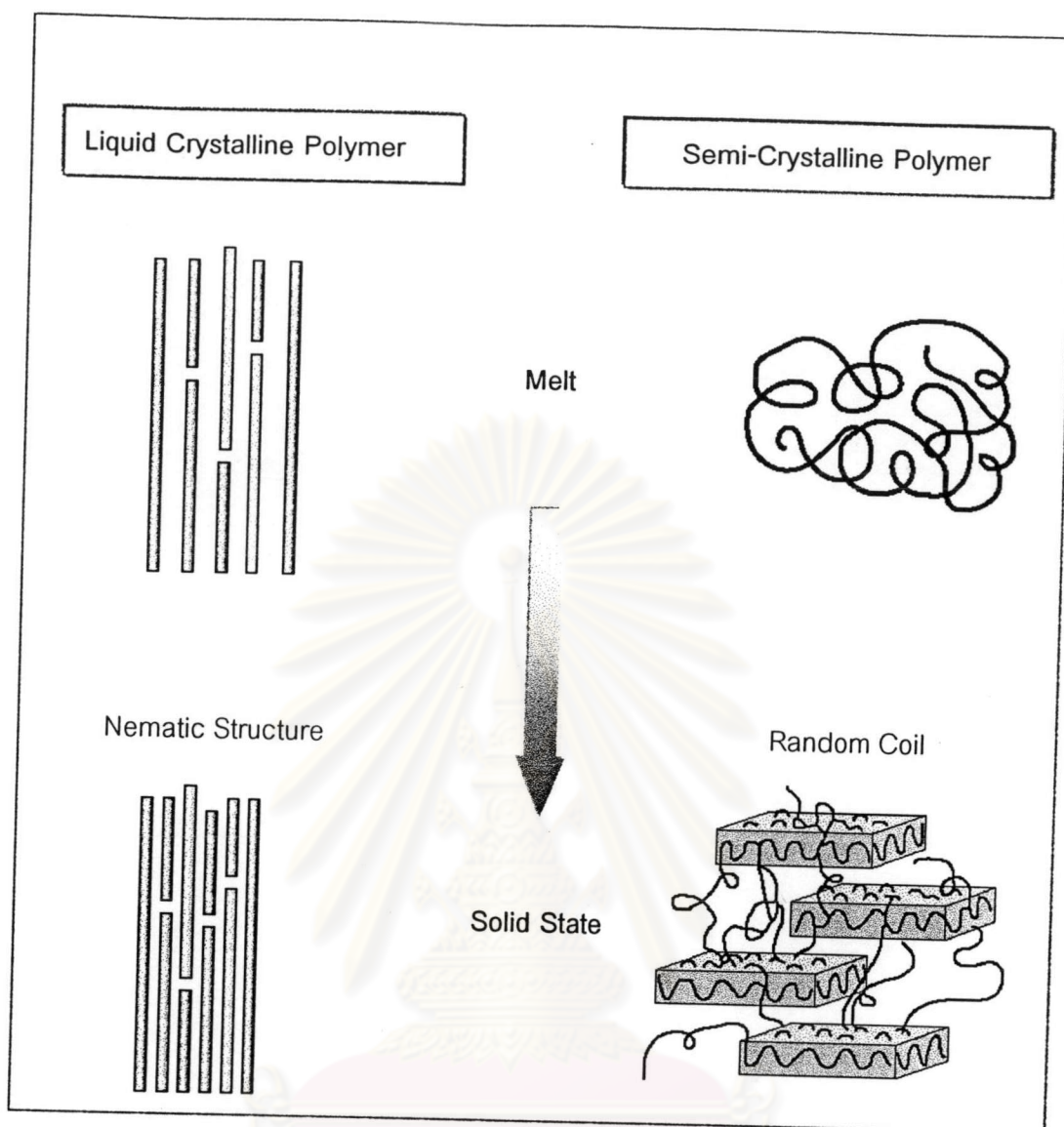**Figure 2.5** Mesogenic position in liquid crystalline polymers [28]

Figure 2.6 Schematic representation of the molecular structure in melt and solid state of liquid crystalline polymer and semi-crystalline polymer [29]

The presence of orientation order in liquid crystal polymers result in anisotropic characters of their properties such as electrical, magnetic, optical, and rheological. It causes LCPs having unique features such as superior chemical stability, dimensional stability, mechanical property, and rheological behavior when compared to conventional polymers such as engineering thermoplastics [27 and 30]. LCPs offer a number of attractive applications: high stiffness and high-strength fiber, precision molded small components, films with excellent barrier properties, novel composites, processing aids in the melt, reversible information storages, endoscopic surgical

instruments, sporting goods, and electro-optical display [30]. Some examples of commercial available of LCPs nowadays are listed in Table 2.2.

Table 2.2 Typical Commercial Thermotropic LCPs [30]

Manufacturer	Chemical Structure
Celanese or Ticona (Vectra[®], Vectran[®])	
DuPont (Zenite[®])	X and Y = -H, -Cl, -Br, -CH$_3$ Z =
Owens-Corning (Montedison/Grandmont)	
Eastman-Kodak (Thermx[®])	
Carbrundum (Amoco) (Xydar[®])	
ICI	R = aromatic diol, carboxylic acid, hydroxy acid (less than 2.5%)

2.6.1.3 The Superior Barrier Feature of LCPs

It is well known that Liquid crystalline polymers are superior barrier polymers to some gases and solvent. Indeed, it is very difficult to find solvent for aromatic polymer such as Vectra. Only a few polymers, i.e. dry-EVOH, PVDC, amorphous Nylon (MXD6), have barrier properties in the same range as LCPs, as clearly seen in Figure 2.7. In addition, LCPs are one of the polymers that are not sensitive to moisture (see Figure 2.8), which is an critical drawback of EVOH and Nylon.
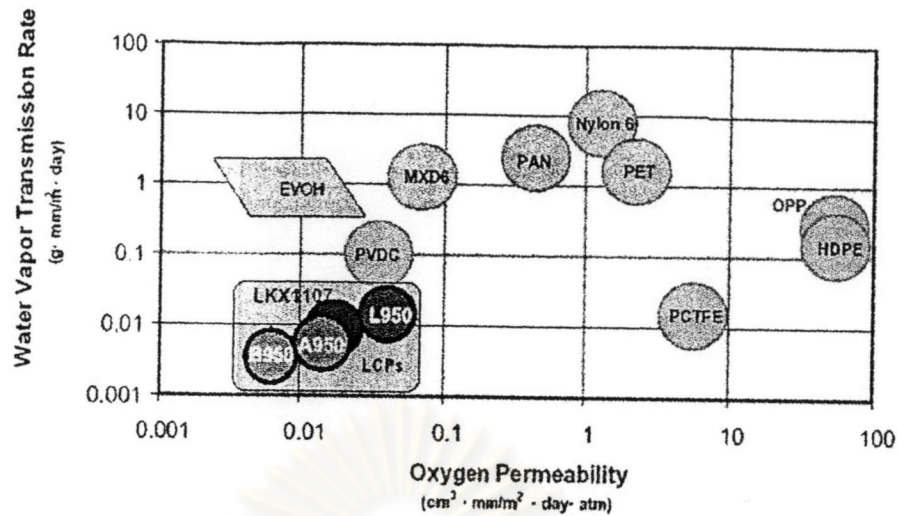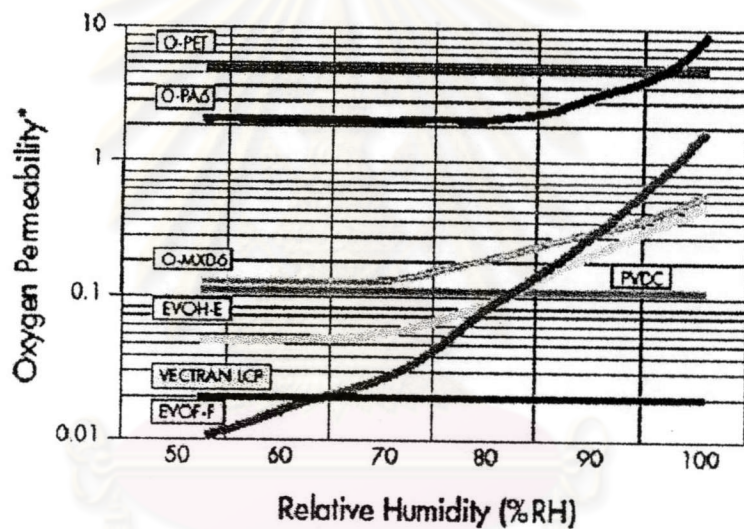
Figure 2.7 Permeability of polymer films [31]

Figure 2.8 Changing of oxygen permeability with relative humidity of polymer films (*in: cc.mil/100 in^2 day. atm) [32]

Study of transport property of LCPs is very rare. One had made by Chiou and Paul in 1987 [33]. LCP films used is fully aromatic copolyester consisting of phenyl naphthyl rings attached together by ester linkage similar to the commercial product Vectra. For comparison, transport properties of polyacrylonitrile (PAN) were also investigated. As expected, the permeabilities of the LCP are generally lower than those of PAN (see Table 2.3). Surprisingly, while the average diffusion coefficients of LCP are 40 times larger than those for PAN, the apparent solubilities are 100 folds smaller. Thus, it could be concluded that the unusual barrier properties of the LCP stem

from exceptionally low solubility rather than intrinsically lower penetrant mobility within the matrix of this rigid polymer chain.

Table 2.3 Comparison of gases transport properties of a wholly aromatic liquid crystalline polymer (Vectra type) with polyacrylonitrile (PAN) at 35°C[33]

Gas	P $\dfrac{(cm^3(STP).cm)}{(cm^2.s.cmHg)} \times 10^{15}$		D $(cm^2/s) \times 10^{10}$		S $(cm^3(STP)/cm^3\ atm)$	
	LCP	PAN	LCP	PAN	LCP	PAN
He	17700	71000	6600	270	0.002	0.20
N_2	3.0	2.9	1.4	0.042	0.0016	0.052
O_2	47	54	7.1	0.14	0.0050	0.29
Ar	10	18	1.5	0.042	0.0054	0.33
CO_2	70	280	0.96	0.023	0.051	9.2

Chiouan Paul also extended the study by investigating the transport properties of LCP consisting of PET/PHB, poly (ethylene terephthalate-co-*p*-oxybensoate), from Eastman Kodak. The objective was to compare the transport properties of LCPs containing different content of PHB of 60 mol% and 80 mol% to those PET. According to previous study, general agreement of the result was observed. The permeability results of LCP containing 60mol%PHB compared to that of 80 mol% showed that the lower permeability can be obtained when PHB content is higher. This is clear that the increased aromatic character of polymer chain results in a decrease in permeability caused primarily by a reduction in the effective diffusivity as seen in Table 2.4.

Table 2.4 Gas transport properties at 35°C for aromatic polyester LCP (PET/PHB) films [2]

Gas	P $\dfrac{(cm^3(STP).cm)}{(cm^2.s.cmHg)} \times 10^{15}$			D $(cm^2/s) \times 10^{10}$			S $(cm^3(STP)/cm^3 \; atm)$		
	PET	PET/PHB 60mol%	PET/PHB 80mol%	PET	PET/PHB 60mol%	PET/PHB 80mol%	PET	PET/PHB 60mol%	PET/PHB 80mol%
N_2	9.7	12	0.5	23	32	11	32	2.9	3.9
O_2	53	11	5	65	83	41	61	10	8.8
CO_2	180	33	12	11	28	12	1300	89	76

In recent year, Ramathal and Lawal [34] have studied the permeability of methanol and toluene vapor through LCP membrane. LCP used was LN001, developmental grade, from Eastman. It was found that the permeability of LCP to methanol and toluene vapor were 2 and 200 times smaller than those of LDPE, respectively. Surprisingly, it was also found that the permeability of toluene was about one order of magnitude higher than methanol eventhough its molecular size is larger. This behavior was also observed in the case of LDPE. The authors suggested that it may be attributed to the more plasticization effect of toluene than methanol or because of the closer of solubility parameter (δ) i.e. PE (δ=8.0 $cal^{1/2}$), toluene (δ=8.91 $cal^{1/2}$), methanol (δ=14.28 $cal^{1/2}$). However, this assumption was not mentioned to the LCP.

The mechanisms by which small molecules permeate through liquid crystalline polymers are not well understood and need more scrutiny. However, the superior barrier feature of this polymer and other potential benefits such as ease of product fabrication, dimension stability, and excellent thermal-mechanical properties convey many interesting aspects of using LCP as a barrier material in packaging [2, 29-30].

2.6.1.4 Rheological Properties of LCP

Rheological behavior of LCPs is extremely complex. In general, viscosity of LCPs is much lower than that of conventional polymers at the comparable molecular weight. The nonlinear viscosity response of LCPs is demonstrated in Figure 2.9. Three

distinct regions are frequently observed. The melt of LCPs contains more domains and is more viscous than small molecule nematics [29]. The polydomain structure of LCPs has a high resistance to flow initially. To overcome the domain structure, a certain stress level must be exceeded initially. Once the material starts to flow, progressive shear thinning prevails at low stress region. After this, the material flows with a higher viscosity because the domains are broken down into smaller sizes with a larger surface area. At higher stress levels, shear thinning predominates again due to the formation of monodomain or homogeneous continuous phase structure.
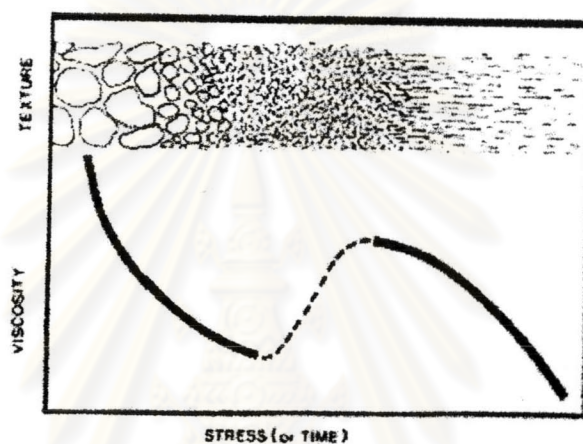

Figure 2.9 Relationship of morphology and rheology of LCP [29]

2.6.1.5 Parameters Affecting to LCPs' Morphology in Blends

2.6.1.5.1 Effect of Flow History

In the polymer processing, the high orientability and the high shear thinning characteristics of thermotropic LCPs are unique and beneficial. Orientation of mesogenic moeties of LCPs occurs readily under a flow field during melt processing. The molecular orientation of a rigid mesogen rod in simple shear and uniaxial extensional or elongational flow fields is depicted in Figure 2.10. For simple shear flow, the difference in the velocities of the end points produces a tumbling or rotational motion of the rod, producing no permanent orientation. In the extensional flow field, the velocity gradient in the flow direction causes the rigid rod to orient itself along the flow field [30]. Thus, the elongational flow is primarily responsible for the orientation of LC molecules

during melt processing. Elongational flow is introduced in polymer processing by drawing-down during fiber extrusion.
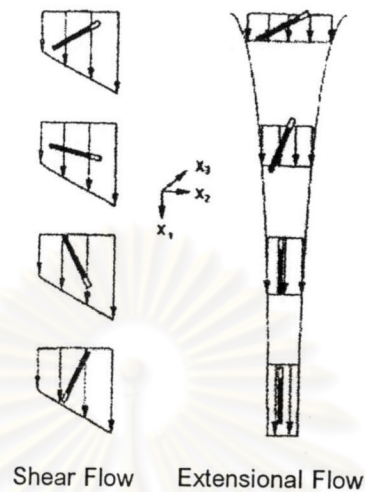

Shear Flow   Extensional Flow

Figure 2.10 Orientability of rigid rod in simple shear and uniaxial extensional flow field [30]

2.6.1.5.2   Effect of Viscosity Ratio

Viscosity ratio is one of critical parameter in morphology control. Viscosity ratio defines as the ratio of the viscosity of the dispersed phase over the viscosity of the matrix [29]. Generally, if the minor component has a lower viscosity than the major one, the minor component will be finely and uniformly dispersed. Conversely, the minor component will be coarsely dispersed if its viscosity is higher than that of the major component.

To achieve the beneficial of in situ reinforcement of LCP as well as high barrier properties, fibrillar structure is preferred to be obtained than droplet structure. It is also well known that the fibrillar structure will be obtained when viscosity ratio of blend system is closed to unity. In spite of instinct viscosity of material itself affecting on viscosity ratio, changing of processing temperature and shear rate of the process may cause the change of viscosity ratio as well.

2.6.1.5.3   Material Content

An amount of studies has been found that fibrillar structure will be obtained after some critical content [29, 36-37]. When the minor phase content lowers than the critical value, dispersed phase will be present in droplet or ellipsoid. In contrast, when the minor phase exceeds some value then the minor phase will be appeared in the form of continuous phase. However, it must be noted that different content values may be observed in different systems and conditions.

2.6.2   Challenges of Blend Containing Liquid Crystalline Polymers in Barrier Development [3]

Although blends containing LCPs have been investigated extensively. Almost all of them have involved the study of mechanical properties improvement. The "in-situ composite" feature makes these blends become interesting. Little has been published concerning the permeability of LCP blends. Thermoplastics used in these studies include polyesters, thermoplastic polyamides, and polyolefins.

2.6.2.1   LCP/Polyester Blends

Motta and colleagues studied the transport properties of PET/Rodrun LC3000 (LCP) blown film [37]. Blend films containing 2, 10, and 30 wt% of LCP were investigated. The LCP was presented almost entirely as spherical droplets at 2 wt% and as droplets and fibrils at 10 and 30 wt%. Permeability to mixture of CO_2, O_2, and N_2 was measured. The films showed the same trend with each gas; after a sharp drop in permeability on addition of 2 wt%LCP, the permeability decreased more gradually, with In *P* linear in wt% LCP. The initial sharp drop, which accounted for about half of the total decrease from 0 to 30 wt% LCP, may be due to an increase in PET crystallinity, with the LCP acting as a nucleating agent.

Modest decrease in oxygen and water vapor permeability has been observed in PEN/LCP blend films. Similar to the PET/Rodun blend film, decreasing of the permeabilities was also observed by increasing crystallinity. This was taken into

account for a decrease in permeability of the blend films. The result indicated that low LCP content is more effective to increase crystallinity of the matrix.

2.6.2.2 LCP/Thermoplastic Polyimide Blends

Limitation of highly anisotropic of LCP in extruded form has been improved by using counter rotating dies [35 and 38]. Moreover, with this technique, a planar or laminar morphology, which is the best structure to receive lowest permeability, can be achieved. Study of LCP/polyimides performed using technique of counter rotating dies showed decreasing in permeability to oxygen and water vapor 8 times and permeability to water vapor over 16 times by addition of 10 wt%LCP, respectively.

The planar morphology is made possible by high transverse shear produced by rotating die, rotating rapidly enough to form layers instead of fibrils. The authors noted that the LCP viscosity must be low comparing to thermoplastic phase. Laminar-flow condition must be maintained in the die as well as the films should be drawn equally in two orthogonal directions after exiting the die, while the blend is partly solidified.

2.6.2.3 LCP/Polyolefin Blends

Because of their wide use as packaging materials, polyolefins have also been blended with LCPs in attempt to improve stiffness and decrease permeability.

Suokas and colleagues [3] developed compatibilized polyolefin-LCP blends containing about 60-70 vol% LCP as the continuous phase. The compatibilizer used was Lotader AX8660 provided by Norsolor. Permeability of blends showed decreasing oxygen permeability from 3000 to 0.6 cm^3/m^2.24 h. atm as the LCP content was increased ~50-60 vol%.

Flodberg and colleagues studied two grade of LCPs , Vectra A950 and RD501, blended with HDPE in blown film extrusion [22] and injection molding [24]. In the case of Blown film they found that LCP with lower viscosity and melting point (RD501) is more preferable to form a more continuous phase in this system. Decreasing of ~90% in oxygen permeability can be obtained when the blends contain 30 wt%LCP. However, some blends with unexpectedly high oxygen permeability were observed in

this study. The authors suggested that it attributed from presence of microvoid in the blend caused by poor adhesion between two phases.

In the case of injection molded samples, the LCP was present in the blend as mixed oriented bands and small spheres at low LCP contents of 4 to 9 wt%LCP, whereas blend with more than 18 wt%LCP show lamellae structure. The decrease in permeability with respect to PE matrix wax about 50% at 9 wt%LCP, and ~90% at 37 wt% of LCP. Comparison between two grades of LCPs showed again that RD 501, having lower viscosity, is better in forming continuous phase of LCP in the matrix, resulting in lower oxygen permeability.

2.7 Polyethylene (PE)

Polyethylene is the most widely used plastic, especially in packaging field. A great variety of types and grades is available, growing steadily as manufacturers find new compositions to specific need.

Polyethylene was first commercial introduction in 1950s. Polyethylene is member of the polyolefin family. Polymerization of polyethylene is addition reaction of ethylene monomer. The chemical structure in Figure 2.11 shows the repeating unit of polyethylene.
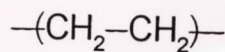
$$-(CH_2-CH_2)-$$

Figure 2.11 Repeating unit of polyethylene

Polyethylene can be linear or branched, homopolymer or copolymer. In the case of copolymer, the other comonomer can be an alkene such as propene, butene, hexene, or octene (see Figure 2.12). These comonomers in polymer chains affect chain packing and crystallization, consequently varying density of polyethylene.

Butene $H_2C=CHCH_2CH_3$

Hexene $H_2C=CH(CH_2)_3-CH_3$

Octene $H_2C=CH(CH_2)_5-CH_3$

Figure 2.12 Alkene comonomer

According to the density difference, polyethylene can be classified into three main categories as follow:

1. High density polyethylene (HDPE)

High density polyethylene is linear polyethylene having density in the range of 0.940 to 0.965 g/cm^3. Generally, HDPE is white and nonpolar polymer. It is one of the most versatile polymers, and is the second most commonly used plastic in the packaging industry.

The molecular chains of HDPE homopolymer are long and straight with little branch. HDPE forms a large fraction of order crystalline regions as it cooled below it melting point. This close packing produces HDPE with crystallinity of 65-90% and contributes to HDPE's good moisture-barrier properties, chemical resistance, and non-transparency.

2. Low density polyethylene (LDPE)

Low density polyethylene is the most widely used packaging plastic. It has a branched structure.

The chain branching in homopolymer LDPE gives this polymer a number of desirable characteristics such as clarity, flexibility, heat sealability, and ease of processing. The actual values of these properties depend on the balance between the molecular weight, molecular weight distribution, and branching. LDPE typically has a density of about 0.910-0.940 g/cm^3.

3. Linear low density polyethylene (LLDPE)

Linear low density polyethylene or LLDPE can be produced as a copolymer having comonomer alkenes such as butene, hexene, or octene.

Molecular weight (Mw) and density (0.916-0.940 g/cm3) control the physical properties of LLDPE. Due to the increased regularity of structure and narrow molecular weight distribution, LLDPE tends to have improved mechanical properties, compared to LDPE at the same density. The greater stiffness results in an increase of 10-15 °C in the melting point of LLDPE compared to LDPE. LLDPE has higher tensile strength, puncture resistance, tear properties, and elongation than LDPE. However, LDPE has better clarity and gloss than LLDPE. LDPE also has better heat seal properties. LDPE and LLDPE are often blended to combine the benefits obtained from both materials, strength of LLDPE and heat seal and processibility of LDPE.

As mentioned before that properties of polyethylene primarily depend on their density, the following table (Table 2.5) shows the properties and trends of properties related to density of polyethylene.

Although, polyethylene has many advantages and is widely used, some limitations including low softening point, low tensile stress, and high gas transmission have made them inappropriate in many applications.

Table 2.5 The properties and trend of properties related to density of polyethylene

Density (g/cm^3)	WVTR (g.µm/m^2.day)	O$_2$ Permeability (cm^3.µm/m^2.day.atm)	Clarity	Tensile Properties
0.910	0.866	275		
0.915	0.779	256		
0.920	0.685	225		
0.925	0.579	201		
0.930	0.465	165		
0.935	0.366	137		
0.940	0.276	104		
0.945	0.244	91.3		
0.950	0.208	76.4		
0.955	0.185	70.1		
0.960	0.145	61.0		

2.8 Relationship of Blends' Structure and Their Properties

2.8.1 Transport Properties: Gas Transport Property Prediction in Multiphase Polymer System

As mentioned earlier, the presence of impermeable dispersed phase creates the longer pathway for gas travel through polymer membrane. This is called "tortuous path concept". The longer pathway is the larger tortuosity, resulting in increasing barrier properties. Tortuosity is primarily dependent upon morphology of the impermeable dispersed phase as seen in Figure 2.2

Tortuosity factor (τ) is the effective path length divided by the actual thickness of the film. Maxwell derived an expression for τ in considering the conductivity of a system in which a conducting phase contains a volume fraction, ϕ_d, of spherical-nonconducting particles, then τ can be express as

$$\tau \cong 1 + \frac{\phi_d}{2}$$
Equation (2.7)

The tortuosity can be used to calculate the permeability of the composite, as written in Equation (2.8).

$$\frac{P_c}{P_m} = \frac{\phi_m}{\tau}$$
Equation (2.8)

Where
P_c is the permeability of the composite

P_m is the permeability of the matrix polymer

ϕ_m is the volume fraction of the matrix polymer

In blends wherein the dispersed polymer is distributed isotropically as uniform spherical particles, for good barrier properties, one has resort to the addition of 30-60% of the barrier polymer. Increasing the content of barrier polymer results in linearly enhancing of barrier properties. However, if the dispersed phases have the form of thin, flat platelets with large areas, then their effectiveness increases significantly. In this case, the pathways become more tortuous, by decreasing the permeation rate.

For nonspherical particles, a term denoting the anisotropy of the filler has to be incorporated. For thin, flat, square platelet, Nielson has modified the tortuosity equation as

$$\tau = 1 + \left[\frac{L}{2W} \right] \cdot \phi_d$$
Equation (2.9)

Where
L is the length of platelet

W is the width of the platelet

ϕ_d is the volume fraction of the dispersed phase

Thus, the permeability P can be calculated as

$$P_c = \frac{P_m(1-\phi_d)}{1+ \left[\dfrac{L}{2W}\right].\phi_d} \qquad \text{Equation (2.10)}$$

Frick extended Maxwell's model to describe the conductivity of a two-phase system in which impermeable ellipsoids are dispersed in a more permeable continuous matrix. According to this model, the permeability of composite materials in which the dispersed phase is distributed as ellipsoids having two equal-length axes perpendicular to the direction of transport can be expressed as

$$P_c = \frac{(P_m + P_d.F)}{(1+F)} \qquad \text{Equation (2.11)}$$

Where
$$F = \left[\frac{\phi_d}{1-\phi_d}\right] . \left[\frac{1}{1+ [1-M].\left[\dfrac{P_d}{P_m}-1\right]}\right] \qquad \text{Equation (2.12)}$$

$$M = \frac{\cos\phi}{\sin^3\phi. \left[\phi - \dfrac{1}{2\sin2\phi}\right]} \qquad \text{Equation (2.13)}$$

and
$$\cos\phi = \frac{W}{L} \qquad \text{Equation (2.14)}$$

In this case, W is the dimension of the axis of the ellipsoid parallel to, and L the dimension perpendicular to, the direction of transport, and ϕ is in radians. When L/W approaches unity, this expression reduces to Maxwell's equation.

The permeability plotted for different L/W values against the volume fraction of the dispersed phase, ϕ_d is given in Figure 2.13 [3].
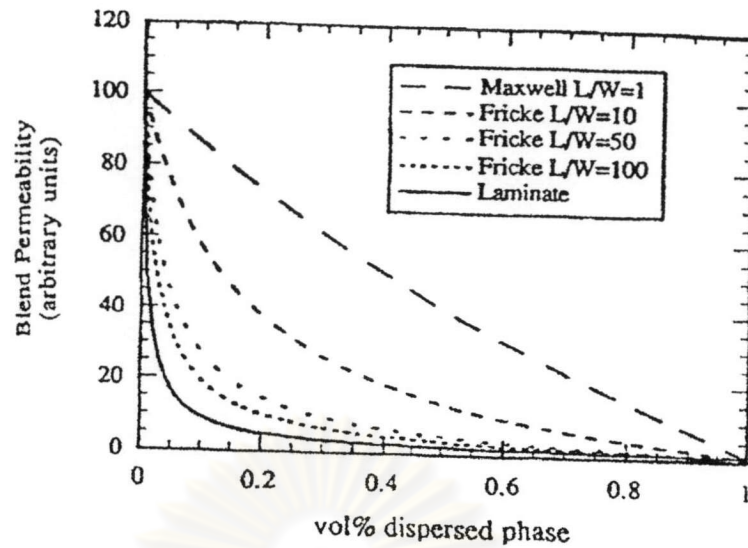
Figure 2.13 Permeability of a hypothetical blend vs. vol% of the dispersed phase, when matrix permeability=100 and dispersed-phase permeability =1 [3].

2.8.2 Mechanical Properties: Application of Composite Theory

The difference in processing condition and material used to create "in-situ composite" produced a wide range of properties. To estimate the modulus, Halpin-Thsi equation seems to be the simplest and most accurate model. This equation as show following in Equation (2.15) was used to calculate the modulus of uniaxially oriented composite materials with fiber reinforcement of uniform aspect ratio.

$$\frac{E_c}{E_m} = \frac{1+ \xi \eta V_f}{1-\eta V_f}$$

Equation (2.15)

(Halpin-Tshi)

Where E_c = modulus of composite

E_m = modulus of matrix

V_f = volume fraction of fibers

and $\xi = \frac{2L}{D}$

Equation (2.16)

$$\eta = \frac{(E_f/E_m)-1}{(E_f/E_m)+ \xi}$$

Equation (2.17)

Where E_f = modulus of fibers

L = length of fiber

D = diameter of fiber

While Halpin-Tshi equation is used to describe elastic modulus of composite reinforcing with different aspect ratio fiber. "Rule of Mixture" or ROM is commonly used to predict the longitudinal modulus of composite having infinite fiber aspect ratio or continuous fiber, and it is given as

$$E_c = V_f E_f + V_m E_m$$

Equation (2.18)

Where V_m = volume fraction of matrix

and $V_m = (1- V_f)$

Figure 2.14 illustrates the example of plot using Halpin-Tsai equation. Relationship of blends structure to their modulus was used to estimate aspect ratio of LCP fibers in blends, which is generally difficult to determine. This equation can be used for estimating aspect ratio as long as the fibers are discontinuous and aligned uniaxially [3].
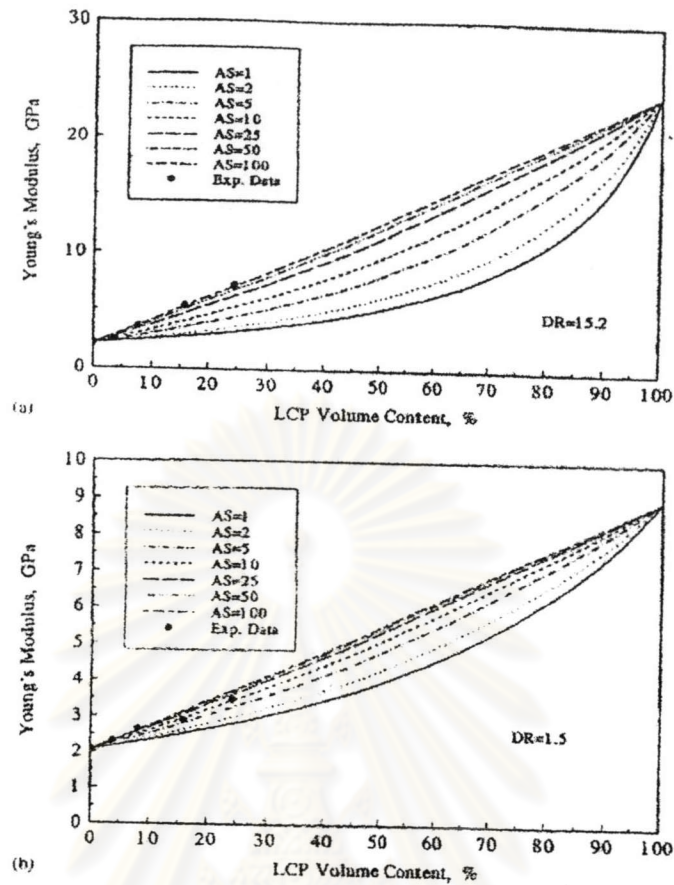
Figure 2.14 Graphical representation of the Halpin–Tsai equation at (a) a draw ratio of 15.2 and (b) a draw ratio of 1.5. Aspect ratios are indicated in the figures: where (*) is experimental data.

A procedure for estimating the tensile strength of in-situ composites has been described by Crevecour and Groeninckx [29]. They proposed two equations for estimating tensile strength at low and high LCP concentrations. At low LCP content, the ductile failure at high strain is dominated by the matrix. Tensile strength will be determined according to:

$$\sigma_c = (1 - V_f)\,\sigma_m \qquad\qquad \text{Equation (2.19)}$$

Where σ_c = tensile strength of composite

σ_m = tensile strength of matrix

On the other hand, at high LCP content, the composite will be dominated by brittle failure at low strain and the tensile properties can be described by

$$\sigma_c = V_f\, \sigma_f + V_m\, \sigma_f\, (E_m/E_f)$$ Equation (2.20)

Where σ_f = tensile strength of fiber

In their work, the experimental data for PS/PPE-Vectra B950 blends were found to be lower than theoretically predicted by Equations (2.19) and (2.20). The authors concluded that prediction should take into account of non-linear stress-strain behavior of material at the high deformation for more accuracy.

2.9 Transmission Rate and Permeability

Since results of transport properties in this research will be reported in term of transmission rate, while information elsewhere generally appears in permeability. Address of the definition and relationship of these two terms may be useful.

Transmission rate is the amount of permeating substance transferred per unit time through a membrane. Transmission rate is generally inversely proportional to the thickness of the membrane and driving force. Double the pressure difference or concentration of a permeant or lower thickness into a half will double the transmission rate.

Permeability is the transmission rate normalized by area and driving force. A standard area is one square meter or 100 square inches, a standard driving force for gas transmission measurement is one atmosphere.