CHAPTER III

EXPERIMENT

Morphologies and barrier properties of LCP/PE blend films were investigated in this study. The effort is to determine the relationship between disperse phase structures, liquid crystalline polymer (LCP), in the blend films as well as their barrier properties. LCP structures were varied depending on processing conditions and compositions. The blends' structures and their developments were investigated by polarized light microscope (OM) and scanning electron microscope (SEM). Oxygen and water vapor transmission rates of the films as well as tensile properties were tested to study the properties of the achieved films.

The following section describes the materials and sample preparation. Blending and film fabrication technique including testing and characterization methods of the blend films are also explained in this chapter. The overview of the experiment is illustrated in the Figure 3.1.

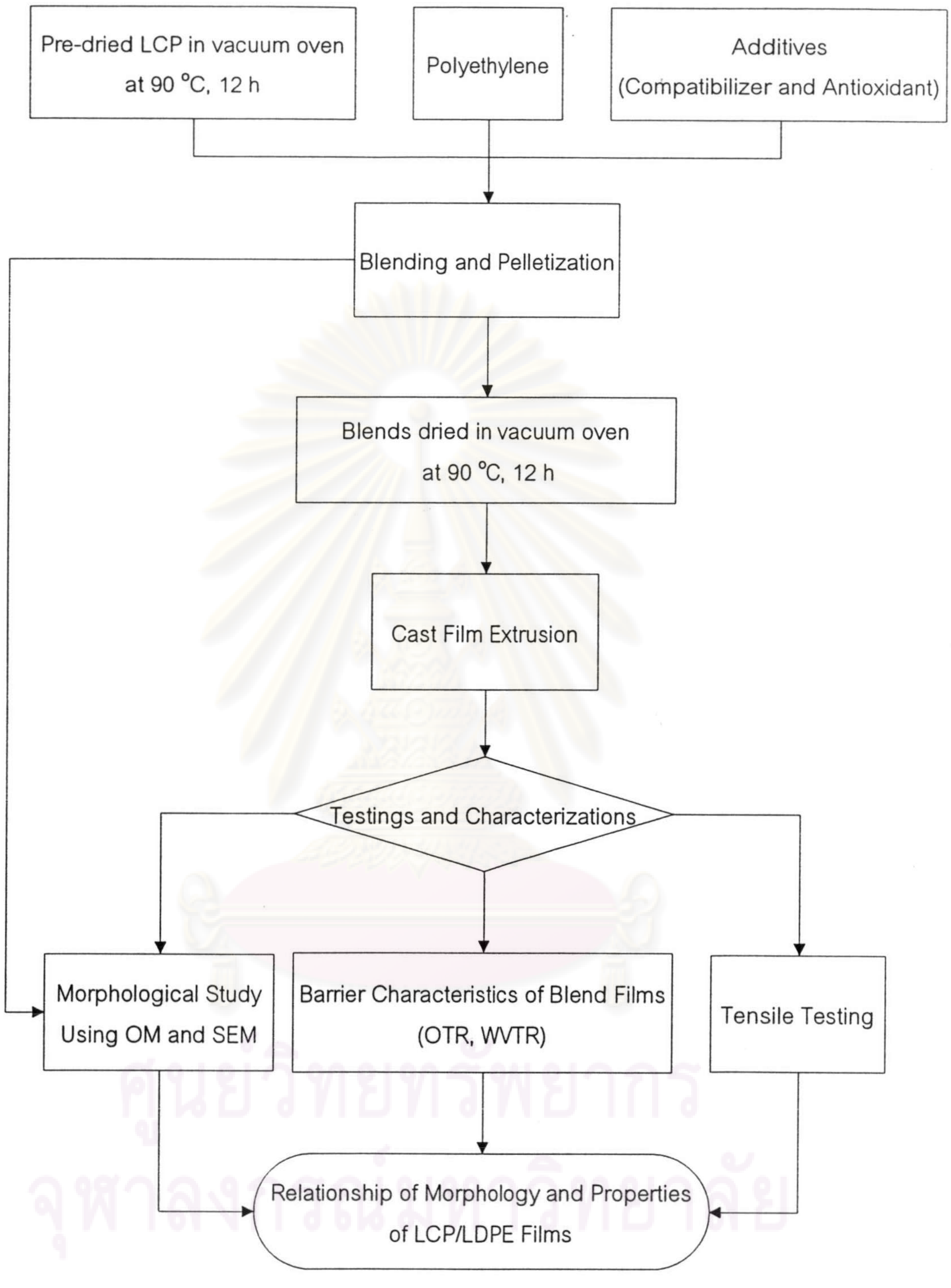


Figure 3.1 The overview of the experiment

3.1 Materials

3.1.1 Liquid Crystalline Polymer (LCP)

Thermotropic liquid crystalline polymer used in this study was an experimental aromatic resin (Vectra®type), namely LKX1107, kindly supported by Ticona (USA). The DSC thermogram of the as-received pellet is showed in Figure 3.2. The exothermic peak revealed mesophase transition at ~170°C, and the endothermic peak of ~ 220 °C was melting temperature. Because of their hygroscopic property, LCP were dried under vacuum at 90 °C for 12 hr before being used.

3.1.2 Polyethylene (PE)

In this study, two types of polyethylene were used as the matrix.

3.1.2.1 Low density polyethylene (LDPE): LDPE was an extrusion grade, LD1902F, obtained from Cementhai Chemical Co. Ltd. (CCC). Melt flow index of the chosen LDPE is 2 g/10min with the density of 0.919 g/cm^3 and its melting temperature is 108 °C.

3.1.2.2 Linear low density polyethylene (LLDPE): LLDPE was used in this study in order to enhance toughness of blends. The chosen grade was 1810 FI provided by Cementhai Chemical Co. Ltd. (CCC). Its melt flow index and density are 1.0 g/10min and 0.918 g/cm^3, respectively.

For more information of these two materials, please see Appendix A.

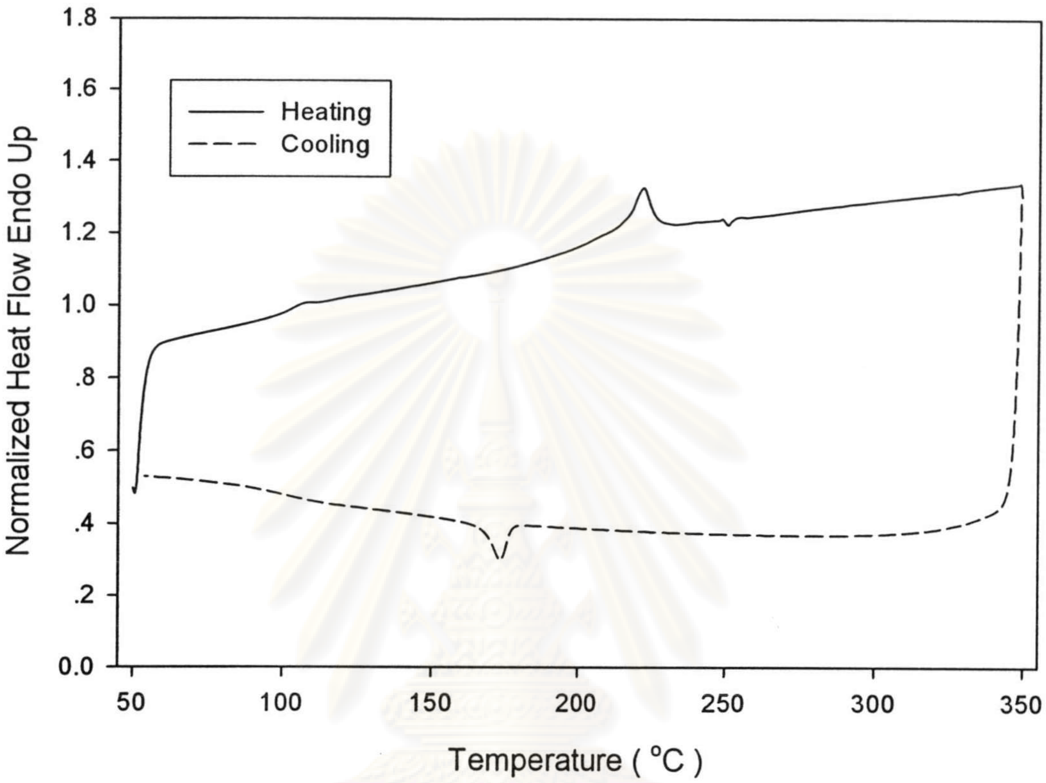


Figure 3.2 DSC thermogram of as-received LCP

3.1.3 Compatibilizer

Nucrel 0903 was used as a compatibilizer. It is an ethylene-methacrylic acid copolymer with 9% of methacrylic acid and provided by Dupont (USA). Chemical structure of this polymer is illustrated in Figure 3.3.

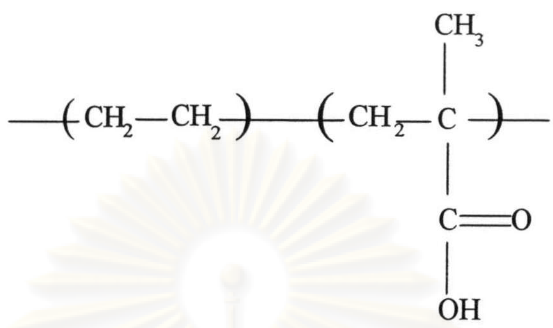


Figure 3.3 The chemical structure of an ethylene-methacrylic acid copolymer

3.1.4 Antioxidant

IRGANOX 1076, a sterically hindered phenolic antioxidant, was use to prevent thermal degradation of polyethylene under high processing temperature. The chemical name of this material is octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate and the chemical structure is depicted in Figure 3.4.

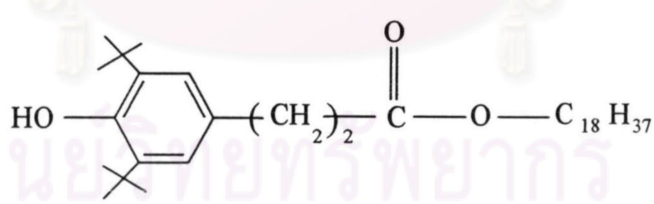


Figure 3.4 The chemical structure of the antioxidant , IRGANOX 1076

3.2 Instruments

The instruments used in this study were listed in the Table 3.1

Table 3.1 The instruments used in the experiment

Instrument	Model	Manufacturer
Single screw extruder	252X	HAAKE
Pelletizer	PP 1 PELLETIZER POSTEX	HAAKE
Chilled roll cast film line	TP 1 TAPE POSTEX	HAAKE
Universal testing machine	4502	Instron
Polarized optical microscope	Axioskop	Ziess
Scanning electron microscope	JSM4510	Joel
Differential scanning calorimeter	DSC 7	Perkin Elmer Metler Toledo
Oxygen permeation analyzer	8500	Illinois

3.3 Methodology

3.3.1 Blending and Pelletization

Various contents of dried LCP, LDPE, and the additives, as listed in Table 3.2, were mechanically blended and extruded using Haake single screw extruder containing a mixing zone (19 mm screw diameter and L/D ~25). Blends were extruded through a rod die of 3 mm diameter and pelletized. Temperature setting from feed zone to die zone was 170-200-230-225 °C. Screw speed of 75 rpm was kept constant for pelletization. Molten extrudate were solidified in water bath before being chopped into pellet by pelletizer as illustrated in Figure 3.5. Pellets were also dried prior to being used for film fabrication.

Table 3.2 List of blends composition

Formula	Content (wt %)			
	LCP	Polyethylene	Compatibilizer	Antioxidant
10LCP0.0Nu	10*	89.9	-	0.1
10LCP0.1Nu	10	89.8	0.1	0.1
10LCP0.5Nu	10	89.4	0.5**	0.1
10LCP1.0Nu	10	88.9	1.0	0.1
10LCP2.0Nu	10	87.9	2.0	0.1
10LCP4.0Nu	10	85.9	4.0	0.1
10LCP10.0Nu	10	79.9	10.0	0.1
5LCP0.5Nu	5	94.4	0.5	0.1
15LCP0.5Nu	15	84.4	0.5	0.1
20LCP0.5Nu	20	79.4	0.5	0.1
30LCP0.5Nu	30	69.4	0.5	0.1
40LCP0.5Nu	40	59.4	0.5	0.1
10LCP0.5NuLL	10	89.4(30LLDPE:70LDPE)	0.5	0.1

*10 wt% of LCP was the effective volume which LCP fibrillation can be achieved [35].

**From the results, 0.5 wt% of compatibilizer is the optimum content and further used for studying the other parameters.

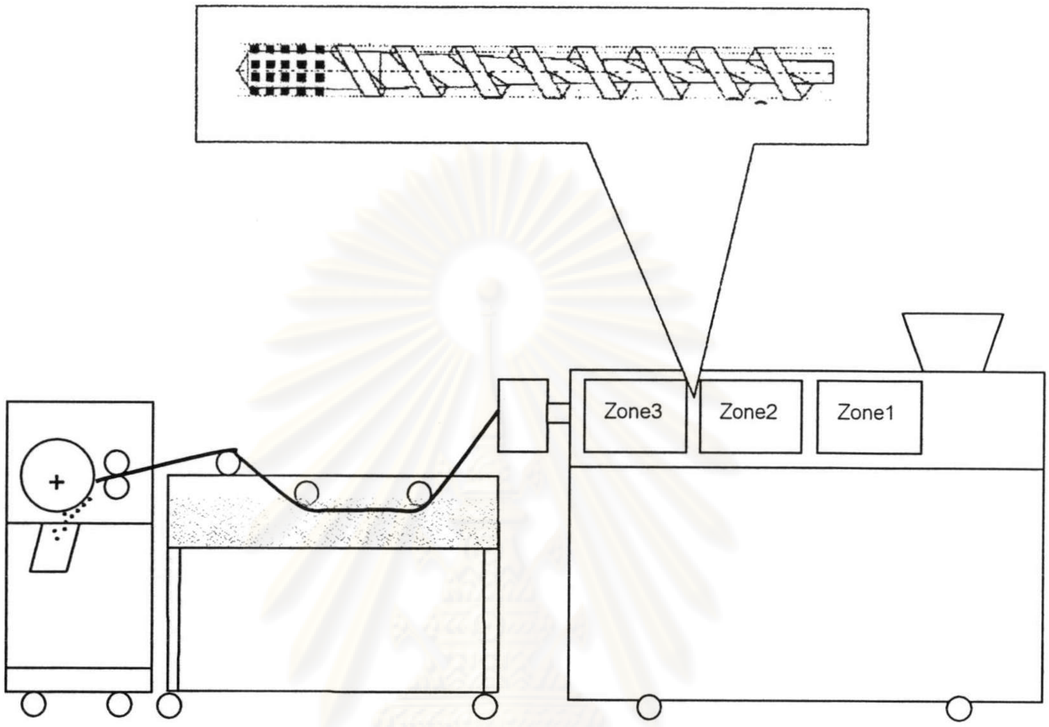


Figure 3.5 Schematic diagram of single screw extruder and pelletization line

3.3.2 Film Fabrication

Cast film extrusion was chosen for film forming in this study. Film fabrication was performed using the same extruder, as previous used in blending section, equipped with a slit die and a cast film line (see Figure 3.6). The gap of the die lip and the width were kept constant at 80 μm and 15 cm, respectively. Chilled rolls' temperatures of cast film haul off were fixed at 45°C. The haul off was positioned as close as possible to the die in order to achieve film with effective width, for the reason of OTR testing. Mobile additional air box was also used for cooling films after coming out from die outlet. Distances of the air box and films were adjusted upon processing conditions and composition of blends to keep films' widths constant.

Processing conditions were varied in order to study their influences on blend film's structures and properties, as fallows:

1. *Processing Temperature Profiles*: The six different temperature profiles were studied. Temperature profiles of the first and second zone were kept constant at 180 °C and 200 °C, respectively. The third zone of the extruder and die temperatures were varied from 220 ^{o}C to 300 ^{o}C, which were identified as profiles T1-T6 (Table 3.3 (1)). Screw speed and post-die drawing or draw ratio (DR) were fixed at 12 rpm and 1.5, respectively. Blends of 10 wt%LCP/LDPE as well as the neat LDPE were produced and investigated. Received films have thickness of approximately 60 μm.

2. *Screw Speeds*: Blend films of 10 wt%LCP were produced at temperature profile T2 and T6 while varied screw speeds of 12, 20, 40, and 60 rpm were performed. Draw ratio of obtained films were also kept constant at 1.5. The neat PE films were also produced for comparison reason. Blend formula of this study are shown in Table 3.3(4).

3. *Post-Die Drawing*: To study the influences of post-die drawing, blend films of 10 wt% and 30 wt%LCP were produced at 4 draw ratios of 1, 1.5, 2, and 3. Draw ratio was defined as the ratio of the die gap's area and cross sectional area of

the final film. The resulting films have 4 different thicknesses i.e. 90, 60, 45, and 30 μm correspondingly. Temperature profiles used were T2 and T6. Details are listed in Table 3.3(5).

4. *Mixing Elements (MEs)*: Mixing elements were considered to be used for enhancing degree of mixing of LCP phase in PE matrix. Mixing elements are usually placed in die adapter, which it positions between die and extruder barrel. In this study, the slit die adapter having 15° converging angle (see figure 3.5) contained two mixing elements of Ross ISG type. The design of these mixing elements is illustrated in Figure 3.5. To study effects of the mixing elements, they were placed in a die adapter of the slit die where molten blend's flow was disturbed. Films of 10 wt%LCP were again produced with 6 different profiles (T1-T6) at the constant take off speed and draw ratio of 1.5 DR. The screw speed in this case must be slightly increased to 14 rpm to receive the similar throughput than that of processing without mixing elements. The resulting films produced with (Table 3.1 (6)) and without (Table 3.1 (1)) mixing elements were compared.

Besides the processing parameters, material composition ,i.e., compatibilizer (Nucrel) content and LCP content were also studies, as summarized in Table 3.3 (2) and 3.3 (3), respectively. It must be noted that study of blend film containing 10 wt%LCP having LLDPE/LDPE as a matrix (10LCP0.5NuLL (Table 3.3 (3)) is for the purpose of enhancing toughness of the blend films.

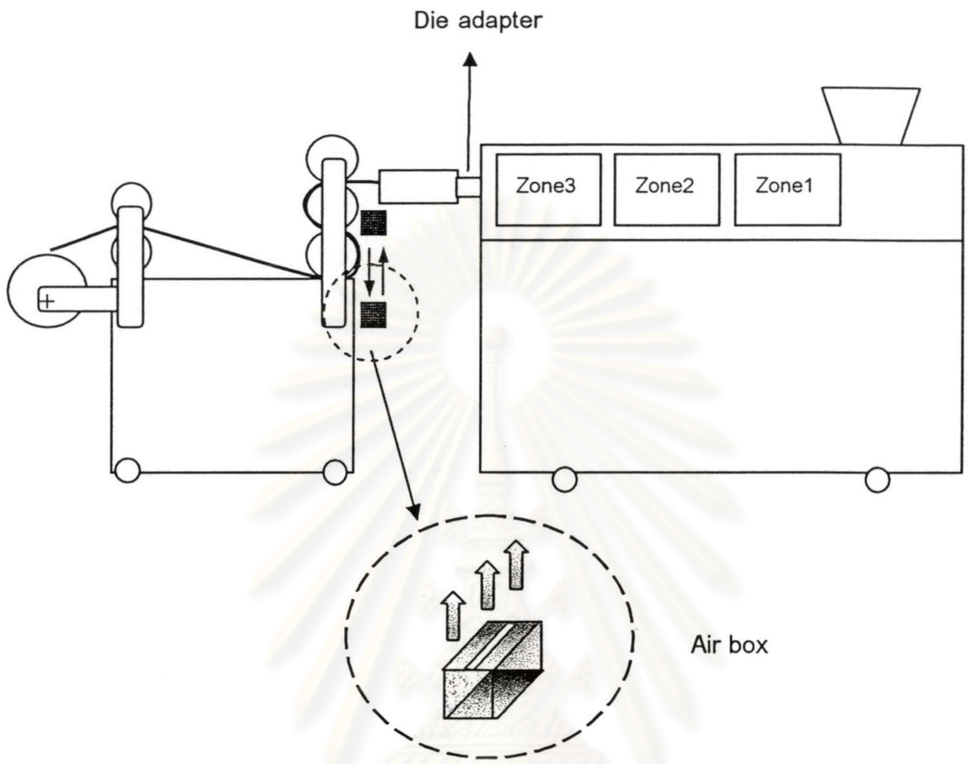
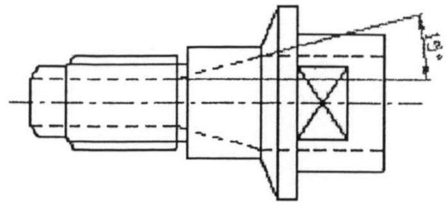
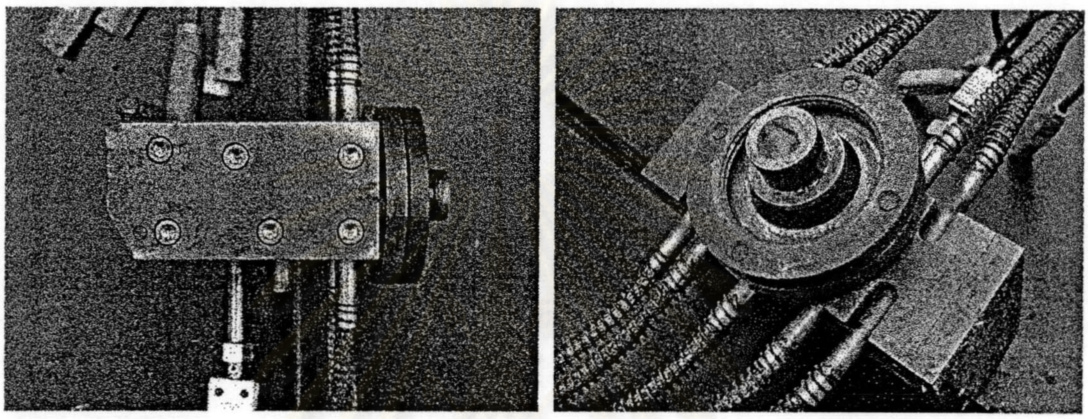


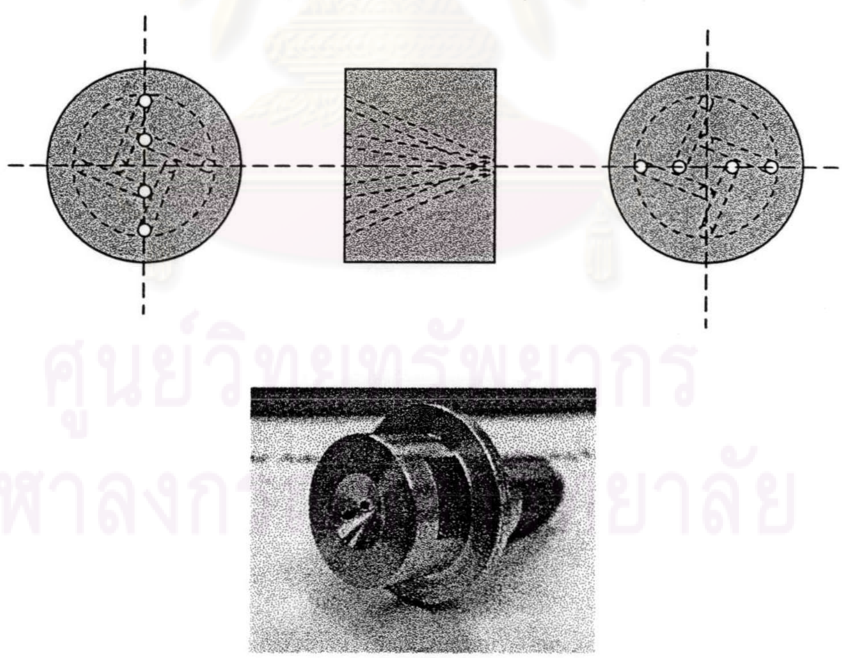
Figure 3.6 Schematic diagram of single screw extruder and cast film line



(a) Die adapter



(b) Die and die adapter



(c) Mixing elements design and die adapter containing mixing elements

Figure 3.7 Drawing of (a) die adapter (b) die and die adapter (c) die adapter with mixing elements

Table 3.3 Compositions and Processing Condition of LCP/PE Blend Films

1. Effect of Processing Temperature Profiles				
Blend Formula	Temperature Profiles (°C) (Extruder zone-1-3 and die)	Screw Speed (RPM)	Post-Die Drawing (DR)	Using of Mixing Elements
10LCP0.5Nu	(T1) 180-200-225-220	12	1.5	No
10LCP0.5Nu	(T2) 180-200-230-225	12	1.5	No
10LCP0.5Nu	(T3) 180-200-235-230	12	1.5	No
10LCP0.5Nu	(T4) 180-200-240-235	12	1.5	No
10LCP0.5Nu	(T5) 180-200-270-270	12	1.5	No
10LCP0.5Nu	(T6) 180-200-300-300	12	1.5	No
2. Effect of Compatibilizer (Nucrel) Content				
Blend Formula	Temperature Profiles (°C) (Extruder zone-1-3 and die)	Screw Speed (RPM)	Post-Die Drawing (DR)	Using of Mixing Elements
10LCP0.0Nu	(T2) 180-200-230-225	12	1.5	No
10LCP0.1Nu	(T2) 180-200-230-225	12	1.5	No
10LCP0.5Nu	(T2) 180-200-230-225	12	1.5	No
10LCP1.0Nu	(T2) 180-200-230-225	12	1.5	No
10LCP2.0Nu	(T2) 180-200-230-225	12	1.5	No
10LCP4.0Nu	(T2) 180-200-230-225	12	1.5	No
10LCP10.0Nu	(T2) 180-200-230-225	12	1.5	No

Table 3.3 Compositions and Processing Condition of LCP/PE Blend Films (Continued)

3. Effect of LCP Content				
Blend Formula	Temperature Profiles (°C) (Extruder zone-1-3 and die)	Screw Speed (RPM)	Post-Die Drawing (DR)	Using of Mixing Elements
5LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
10LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
15LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
20LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
30LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
40LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
10LCP0.5NuLL	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
4. Effect of Screw Speed				
Blend Formula	Temperature Profiles (°C) (Extruder zone-1-3 and die)	Screw Speed (RPM)	Post-Die Drawing (DR)	Using of Mixing Elements
10LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
10LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	20	1.5	No
10LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	40	1.5	No
10LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	60	1.5	No

Table 3.3 Compositions and Processing Condition of LCP/PE Blend Films (continued)

5. Effect of Post-Die Drawing				
Blend Formula	Temperature Profiles (°C) (Extruder zone-1-3 and die)	Screw Speed (RPM)	Post-Die Drawing (DR)	Using of Mixing Elements
10LCP0.5Nu 30LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1	No
10LCP0.5Nu 30LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	1.5	No
10LCP0.5Nu 30LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	2	No
10LCP0.5Nu 30LCP0.5Nu	(T2) 180-200-230-225 (T6) 180-200-300-300	12	3	No
6. Effect of Using of Mixing Elements				
Blend Formula	Temperature Profiles (°C) (Extruder zone-1-3 and die)	Screw Speed (RPM)	Post-Die Drawing (DR)	Using of Mixing Elements
10LCP0.5Nu	(T1) 180-200-225-220	12	1.5	Yes
10LCP0.5Nu	(T2) 180-200-230-225	12	1.5	Yes
10LCP0.5Nu	(T3) 180-200-235-230	12	1.5	Yes
10LCP0.5Nu	(T4) 180-200-240-235	12	1.5	Yes
10LCP0.5Nu	(T5) 180-200-270-270	12	1.5	Yes
10LCP0.5Nu	(T6) 180-200-300-300	12	1.5	Yes

3.4 Characterizations and Testings

The resulting films' morphology was examined under polarized light optical microscope (OM) and scanning electron microscope (SEM). Properties of the neat and blend films, i.e., barrier properties to oxygen gas and water vapor and tensile performances were tested.

3.4.1 Morphology Study

Morphology of Blend films were investigated using 2 techniques

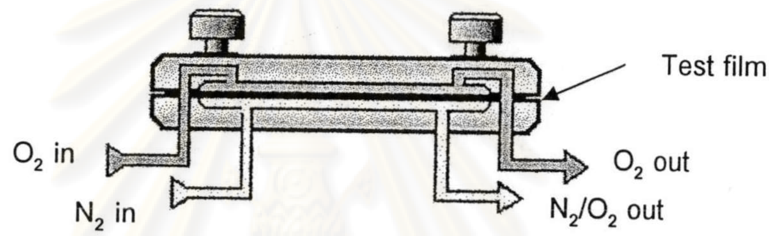
3.4.1.1 *Polarized Light Optical Microscope (OM):* Optical microscope used in this study was Axioskop, Ziess. Specimens were prepared by placing blend film sample between two glass slides and then heated up to temperature of ~160°C in order to melt PE matrix. The present LCP structure during processing could then be revealed. Specimens were observed with 100x and 200x magnifications. Photographs were taken using an attached camera (model MC 100 Spot, Ziess).

3.4.1.2 *Scanning Electron Microscope (SEM)*: The microstructure of LCP/PE blend films was observed under a Joel scanning electron microscope, model JSM5410, using an accelerating voltage of 15 kV. Blend films were fractured in liquid nitrogen. Prior to examination, facture surfaces were sputter coated with gold for enhanced surface conductivity.

3.4.2 Barrier Properties Testing

Barrier characters of LCP/PE film were examined by measuring oxygen transmission rate and water vapor transmission rate as following described.

3.4.2.1 ***Oxygen Transmission Rate (OTR):*** OTR values were determined at temperature of ~23°C and 0 %RH using oxygen permeation analyzer (Illinois, model 8500) as shown in Figure 3.6. Film specimens having 100 mm^2 area were tested. At least three replicates for each film sample were averaged.



(a) Operational principle diagram

(b) Oxygen permeation analyzer

Figure 3.8 Schematic diagram of (a) an operational principle of oxygen transmission rate measurement and (b) oxygen permeation analyzer, the instrument

3.4.2.2 *Water Vapor Transmission Rate (WVTR)*: Measurements of WVTR of LCP/PE films were performed following the ASTM E96-95. It is the traditional gravimetric cup method (see Figure. 3.7). Film specimens were mounted over a test dish containing dried silica gel. Films' active areas for measuring were 0.00312 m^2 and the rest of the film specimens were sealed to the flange of the dish with paraffin. Initial weights of the prepared dish were recorded prior to keep in controlled atmosphere. The conditions were 35 °C and 90 % RH. Weight changes were periodically measured at every 24 hr until the steady state was reached. Thus, the water vapor transmission rate can be calculated from the slope of weight gain vs. time curve.

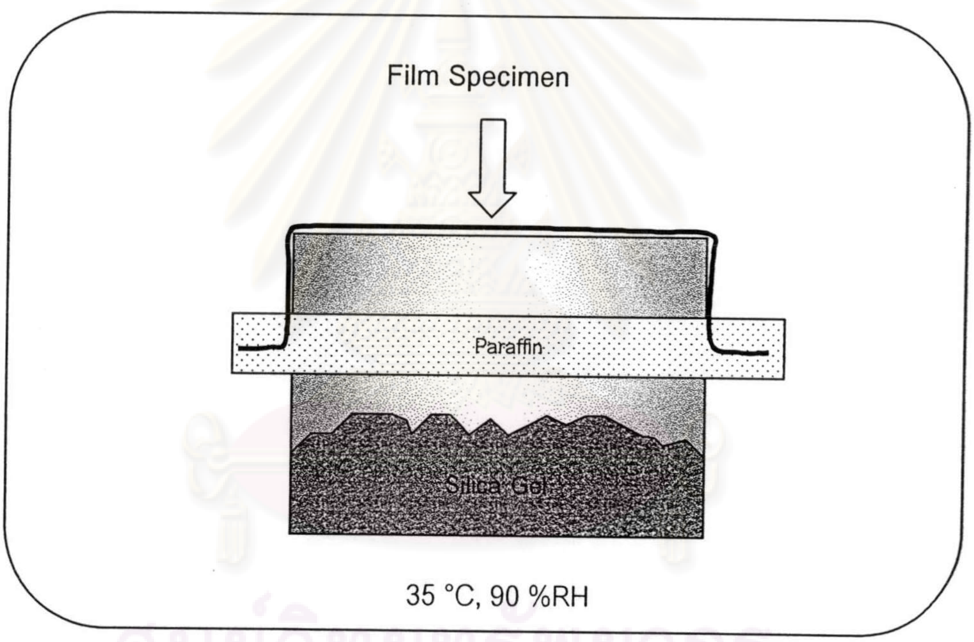


Figure 3.9 Test dish used in measuring water vapor transmission rates by the gravimetric method

3.4.3 Tensile Testing

LCP/PE films, both machine direction (MD) and transverse direction (TD), were tested on an Instron universal testing machine, model 4502, according to the ASTM D-882 for thin plastic sheet. Film specimens for modulus determination were rectangular with a 50 mm gauge length and 25.4 mm width. Load cell of 100 N and crosshead speed of 10 mm/min were used. Rectangular specimens for yield measurement having 15 mm width were tested using crosshead speed of 100 mm/min. Yong's modulus, yield stress, yield strain, and toughness were collected for each specimen. Data of at least 5 specimens were averaged using Instron software.