CHAPTER IV

EXPERIMENTAL

In this chapter, the raw materials, mixing techniques and experimental tests that have been performed in this research will be briefly explained.

4.1 Materials

4.1.1 High Density Polyethylene (HDPE)

Unstabilized high density polyethylene (film grade) is used. It is manufactured by Bangkok Polyethylene Public Company Limited. Its characteristics are shown in Table 4.1.

Table 4.1 : The characteristics of unstabilized HDPE powder.

Characteristics of HDPE	Value
Melt Flow Rate (g/10 min)	0.1465 - 0.2273
Lightness Corrected	83.5
Viscosity (Pa.s) at 600 s^{-1}	450
Density (g/cm^3)	0.9544 - 0.9566

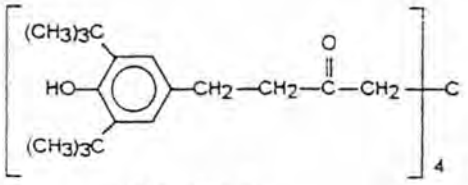
4.1.2 Additives

The additives used in this research are commercial products. A list of both the primary and the secondary antioxidants, hindered amine light stabilizer (HALS) and optical brightening agent is presented in Table 4.2.

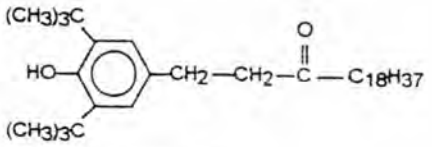
Table 4.2 : The antioxidants, hindered amine light stabilizer and optical brightener used in the present study.

TYPE	DESIGNATION	CHEMICAL NAME	APPEARANCE
Primary antioxidant Phenolic type	PATHP	Pentaerythrityl-tetrakis [3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate]	White to slightly yellowish, Crystalline powder
	ODHP	Octadecyl 3-(3,5-di-tert.butyl-4-hydroxy phenyl)-propionate	White to slightly yellowish free flowing powder
	DAT	di-α-Tocopherol	Yellow to yellowish brown, clear, viscous oil
Secondary antioxidant Thioester type	DLTDP	Dilauryl thiodipropionate	White crystals
	DSTDP	Distearyl thiodipropionate	White crystals
Blended antioxidant	Blended AO	Blended of PATHP and tris-(2,4-di-tert. butylphenyl)-phosphite 1:2 by weight.	Gummy agglomerate
Hindered Amine Light Stabilizer (HALS)	Blended HALS	Blended of Poly[[6-[(1,1,3,3-tetramethylbutyl) amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl [(2,2,6,6-tetramethyl-4-piperidinyl)imino]] and 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol at 1:1 by weight.	White to slightly yellow granule
Optical Brightening Agent (OBA)	OBA	2,5-thiophenediylbis(5-tert-butyl-1,3-benzoxazole)	Yellow, greenish powder

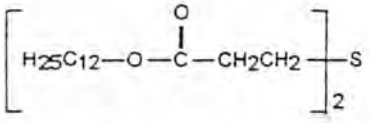
Figure 4.1 shows the chemical structure of the antioxidants, light stabilizer and optical brightening agent used in the present study.



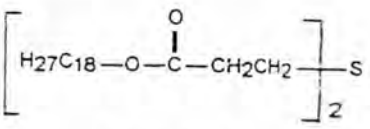
Phenolic-1



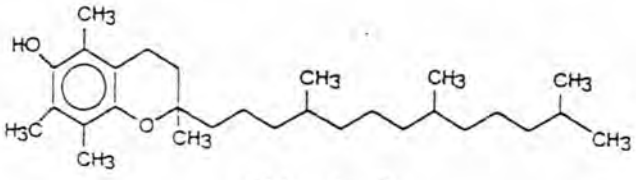
Phenolic-2



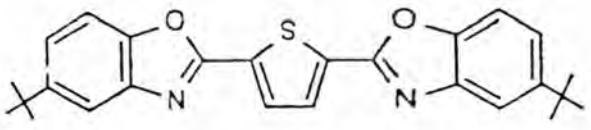
Thioester-1



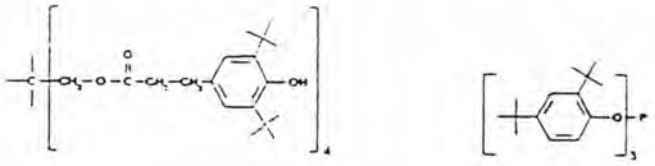
Thioester-2



Thioester-3

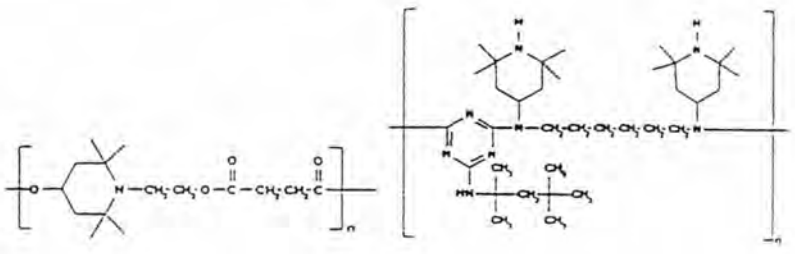


OBA



1 : 2

Blended Antioxidant



1 : 1

HALS

Figure 4-1 : The chemical structure of all additives used in the present study.

4.2 Experimental Design

The designed formulation of HDPE compounded with the selected additives in the present study was based on the percentage by weight of the HDPE. Hindered amine light stabilizer (HALS) was added to prevent photo-oxidation caused by the ultraviolet component of light at a constant concentration of 0.25%. Central composite rotatable (CCR) experimental design was used to vary three additives quantity as follows.

a) primary antioxidants of phenolic type used in the present study (PATHP, ODHP and DAT) were varied between 0.0204 to 0.08%.

b) secondary antioxidants of thioester type (DLTDP and DSTDP) were varied between 0.0204 to 0.08%

c) blended antioxidant (Blended AO) was varied between 0.02 to 0.08%

d) optical brightening agent (OBA) was varied between 0.0005 to 0.001%

The quantities of the above additives were varied at five levels. In the CCR experimental design, they were designated codes as -1.682, -1, 0, +1 and +1.682. Blended antioxidant was mixed with OBA, HALS and HDPE in accordance with the 13 formulae shown in Table 4.3. Then a primary antioxidant and a secondary antioxidant were chosen and mixed with the OBA, HALS and HDPE. As a consequence, there are 6 sets of experimentals each with 20 formulae as show in Tables 4.4 to 4.9. The properties of the compounded HDPE for each formula was tested, each set of data was analyzed statistically.

Table 4.3 : Designed formulae of compounded HDPE with Blended AO, OBA and Blended HALS.

Formulae	Concentration (% by weight)		
	Blend AO	OBA	Blended HALS
A01	0.0200	0.00050	0.25
A02	0.0800	0.00050	0.25
A03	0.0200	0.00100	0.25
A04	0.0800	0.00100	0.25
A05	0.0076	0.00075	0.25
A06	0.0924	0.00075	0.25
A07	0.0500	0.00040	0.25
A08	0.0500	0.00110	0.25
A09	0.0500	0.00075	0.25
A10	0.0500	0.00075	0.25
A11	0.0500	0.00075	0.25
A12	0.0500	0.00075	0.25
A13	0.0500	0.00075	0.25

Table 4.4 : Designed formulae of compounded HDPE with PATHP, DLTDP, OBA and Blended HALS.

Formulae	Concentration (% by weight)			
	PATHP	DLTDP	OBA	Blended HALS
B01	0.0204	0.0204	0.00050	0.25
B02	0.0800	0.0204	0.00050	0.25
B03	0.0204	0.0800	0.00050	0.25
B04	0.0800	0.0800	0.00050	0.25
B05	0.0204	0.0204	0.00100	0.25
B06	0.0800	0.0204	0.00100	0.25
B07	0.0204	0.0800	0.00100	0.25
B08	0.0800	0.0800	0.00100	0.25
B09	0.0000	0.0502	0.00075	0.25
B10	0.0100	0.0502	0.00075	0.25
B11	0.0502	0.0000	0.00075	0.25
B12	0.0502	0.0100	0.00075	0.25
B13	0.0502	0.0502	0.00033	0.25
B14	0.0502	0.0502	0.00117	0.25
B15	0.0502	0.0502	0.00075	0.25
B16	0.0502	0.0502	0.00075	0.25
B17	0.0502	0.0502	0.00075	0.25
B18	0.0502	0.0502	0.00075	0.25
B19	0.0502	0.0502	0.00075	0.25
B20	0.0502	0.0502	0.00075	0.25

Table 4.5 : Designed formulae of compounded HDPE with PATHP, DSTDP, OBA and Blended HALS.

Formulae	Concentration (% by weight)			
	PATHP	DSTDP	OBA	Blended HALS
C01	0.0204	0.0204	0.00050	0.25
C02	0.0800	0.0204	0.00050	0.25
C03	0.0204	0.0800	0.00050	0.25
C04	0.0800	0.0800	0.00050	0.25
C05	0.0204	0.0204	0.00100	0.25
C06	0.0800	0.0204	0.00100	0.25
C07	0.0204	0.0800	0.00100	0.25
C08	0.0800	0.0800	0.00100	0.25
C09	0.0000	0.0502	0.00075	0.25
C10	0.0100	0.0502	0.00075	0.25
C11	0.0502	0.0000	0.00075	0.25
C12	0.0502	0.0100	0.00075	0.25
C13	0.0502	0.0502	0.00033	0.25
C14	0.0502	0.0502	0.00117	0.25
C15	0.0502	0.0502	0.00075	0.25
C16	0.0502	0.0502	0.00075	0.25
C17	0.0502	0.0502	0.00075	0.25
C18	0.0502	0.0502	0.00075	0.25
C19	0.0502	0.0502	0.00075	0.25
C20	0.0502	0.0502	0.00075	0.25

Table 4.6 : Designed formulae of compounded HDPE with ODHP,DLTDP, OBA and Blended HALS.

Formulae	Concentration (% by weight)			
	ODHP	DLTDP	OBA	Blended HALS
D01	0.0204	0.0204	0.00050	0.25
D02	0.0800	0.0204	0.00050	0.25
D03	0.0204	0.0800	0.00050	0.25
D04	0.0800	0.0800	0.00050	0.25
D05	0.0204	0.0204	0.00100	0.25
D06	0.0800	0.0204	0.00100	0.25
D07	0.0204	0.0800	0.00100	0.25
D08	0.0800	0.0800	0.00100	0.25
D09	0.0000	0.0502	0.00075	0.25
D10	0.0100	0.0502	0.00075	0.25
D11	0.0502	0.0000	0.00075	0.25
D12	0.0502	0.0100	0.00075	0.25
D13	0.0502	0.0502	0.00033	0.25
D14	0.0502	0.0502	0.00117	0.25
D15	0.0502	0.0502	0.00075	0.25
D16	0.0502	0.0502	0.00075	0.25
D17	0.0502	0.0502	0.00075	0.25
D18	0.0502	0.0502	0.00075	0.25
D19	0.0502	0.0502	0.00075	0.25
D20	0.0502	0.0502	0.00075	0.25

Table 4.7 : Designed formulae of compounded HDPE with ODHP, DSTDP, OBA and Blended HALS.

Formulae	Concentration (% by weight)			
	ODHP	DSTDP	OBA	Blended HALS
E01	0.0204	0.0204	0.00050	0.25
E02	0.0800	0.0204	0.00050	0.25
E03	0.0204	0.0800	0.00050	0.25
E04	0.0800	0.0800	0.00050	0.25
E05	0.0204	0.0204	0.00100	0.25
E06	0.0800	0.0204	0.00100	0.25
E07	0.0204	0.0800	0.00100	0.25
E08	0.0800	0.0800	0.00100	0.25
E09	0.0000	0.0502	0.00075	0.25
E10	0.0100	0.0502	0.00075	0.25
E11	0.0502	0.0000	0.00075	0.25
E12	0.0502	0.0100	0.00075	0.25
E13	0.0502	0.0502	0.00033	0.25
E14	0.0502	0.0502	0.00117	0.25
E15	0.0502	0.0502	0.00075	0.25
E16	0.0502	0.0502	0.00075	0.25
E17	0.0502	0.0502	0.00075	0.25
E18	0.0502	0.0502	0.00075	0.25
E19	0.0502	0.0502	0.00075	0.25
E20	0.0502	0.0502	0.00075	0.25

Table 4.8 : Designed formulae of compounded HDPE with DAT, DLTDP, OBA and Blended HALS.

Formulae	Concentration (% by weight)			
	DAT	DLTDP	OBA	Blended HALS
F01	0.0204	0.0204	0.00050	0.25
F02	0.0800	0.0204	0.00050	0.25
F03	0.0204	0.0800	0.00050	0.25
F04	0.0800	0.0800	0.00050	0.25
F05	0.0204	0.0204	0.00100	0.25
F06	0.0800	0.0204	0.00100	0.25
F07	0.0204	0.0800	0.00100	0.25
F08	0.0800	0.0800	0.00100	0.25
F09	0.0000	0.0502	0.00075	0.25
F10	0.0100	0.0502	0.00075	0.25
F11	0.0502	0.0000	0.00075	0.25
F12	0.0502	0.0100	0.00075	0.25
F13	0.0502	0.0502	0.00033	0.25
F14	0.0502	0.0502	0.00117	0.25
F15	0.0502	0.0502	0.00075	0.25
F16	0.0502	0.0502	0.00075	0.25
F17	0.0502	0.0502	0.00075	0.25
F18	0.0502	0.0502	0.00075	0.25
F19	0.0502	0.0502	0.00075	0.25
F20	0.0502	0.0502	0.00075	0.25

Table 4.9 : Designed formulae of compounded HDPE with DAT, DSTDP, OBA and Blended HALS.

Formulae	Concentration (% by weight)			
	DAT	DSTDP	OBA	Blended HALS
G01	0.0204	0.0204	0.00050	0.25
G02	0.0800	0.0204	0.00050	0.25
G03	0.0204	0.0800	0.00050	0.25
G04	0.0800	0.0800	0.00050	0.25
G05	0.0204	0.0204	0.00100	0.25
G06	0.0800	0.0204	0.00100	0.25
G07	0.0204	0.0800	0.00100	0.25
G08	0.0800	0.0800	0.00100	0.25
G09	0.0000	0.0502	0.00075	0.25
G10	0.0100	0.0502	0.00075	0.25
G11	0.0502	0.0000	0.00075	0.25
G12	0.0502	0.0100	0.00075	0.25
G13	0.0502	0.0502	0.00033	0.25
G14	0.0502	0.0502	0.00117	0.25
G15	0.0502	0.0502	0.00075	0.25
G16	0.0502	0.0502	0.00075	0.25
G17	0.0502	0.0502	0.00075	0.25
G18	0.0502	0.0502	0.00075	0.25
G19	0.0502	0.0502	0.00075	0.25
G20	0.0502	0.0502	0.00075	0.25

4.3 Multiple Extrusion

Each additive was dry blended with HDPE powder according to the formulations designed in Tables 4.3 to 4.9. Compounding was performed by using a single screw extruder at a speed of 60 rpm to allow homogeneous dispersion of the mixing additives. The compounding temperature was set at 200°C, 220°C, 220°C 220°C and 220°C respectively from the feed zone to the die zone. Reprocessing of the compounded pellets from the first to fifth passes was conducted by using a single screw extruder. The speed of the extruder screw was 60 rpm while the barrel temperature was kept constant at 200°C, 220°C, 250°C, 250°C and 250°C respectively, from the feed to the die zone. After each pass, an amount of the chopped extrudate was set aside for evaluation of its melt properties, color stability and oxidative stability.

4.4 Testing of Thermal and Physical Properties

4.4.1 Differential Scanning Calorimetry (DSC) Analysis

DSC technique monitors the changes in the enthalpy of a polymeric sample as a function of temperature. DSC is mainly used for the study of physical transitions although reactions such as degradation, polymerization, oxidation and chemical reactions can also be studied. Other important applications of DSC to polymers and intermediates include heat capacity, the degree of crystallinity and the purity measurements. Melting temperatures are frequently used for polymer identification on the basis that each polymer shows its characteristic melting endotherm in pure polymer or an incompatible mixture [17].

Each compounded formulation was compression moulded to form a thin film of 250 μm in thickness. The compounded formulation was heated at 170°C for 3 minutes without any pressure. Then a pressure of 100 kg/cm^3 was introduced. After a full pressure has been achieved, the heating was continued for 3 minutes. At the end of the heating period, the hot-pressed film was air-cooled to ambient temperature. The compressed film was then cut to form a circular disk of 5.4 mm in diameter.

DSC thermograms were recorded on a Perkin Elmer Instrument. Each compounded formulation was weighed and placed in an aluminium pan without cover nor encapsulation. The isothermal method was performed on the DSC during the analysis. The sample was heated from 50°C to a constant temperature of 200°C at a heating rate of 80°C/min. The heating was performed under N_2 atmosphere in which N_2 gas was purged and allowed to flow in at a pressure of 20 psi. When the set temperature has been reached, the purged gas was switched off and oxygen gas was then allowed to flow in at a pressure of 3 psi. This operation was performed until the steepest point of the exotherm had been achieved on the thermalscan. The Oxidative-Induction Time (OIT) was measured at the time from the start of the heating at 50°C to the appearance of the first exotherm. The OIT result represents the resistance to oxidative decomposition.

4.4.2 Melt Flow Rate (MFR) Analysis

The viscosity and the flow characteristics of thermoplastics are some of the major influences on the processing methods and he pelated mold design. Viscosity is defined simply as refers the resistance of a liquid to flow. The Melt

flow rate is the inverse of viscosity; a high melt flow rate indicates a low viscosity [18].

Measurement of the melt flow rate (MFR) is commonly used to detect the change of the original molecular weight and the molecular weight distribution of polymer during processing. An Auto Melt Flow Indexer is shown schematically in Figure 4.2.

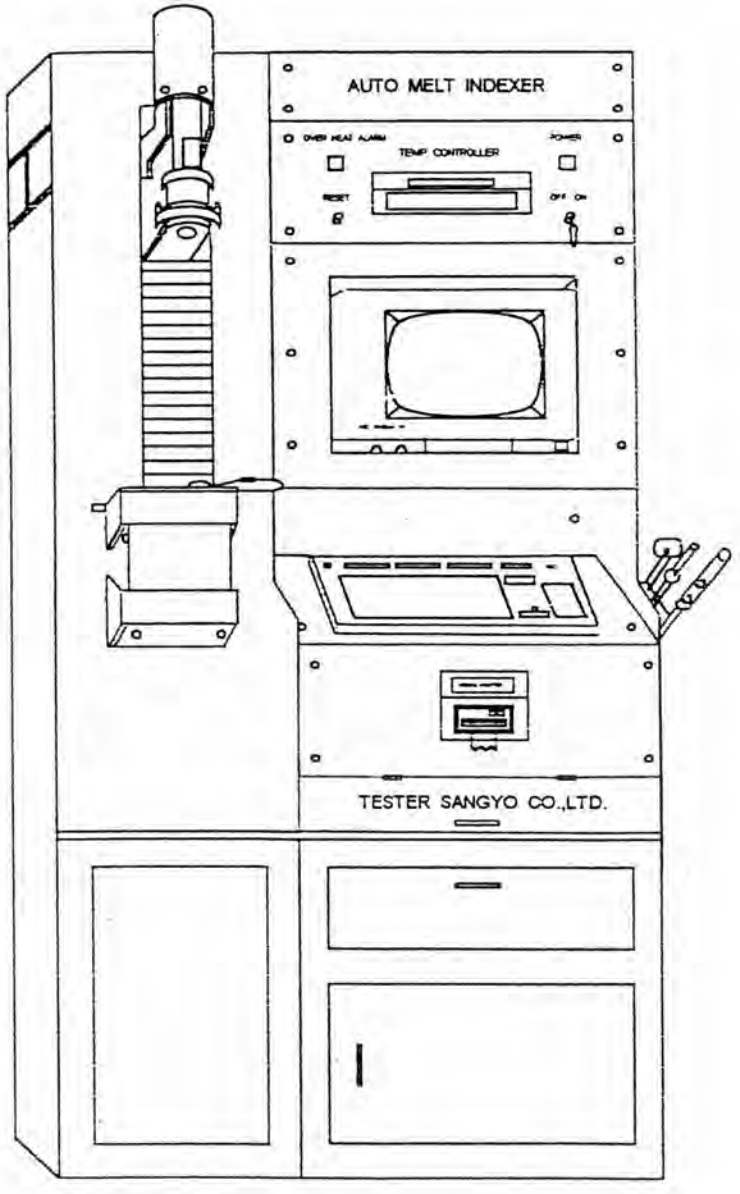


Figure 4.2 : The schematic diagram of an Auto Melt Indexer.

The melt flow rate is monitored by an Auto Melt Indexer in accordance with the procedure described in ASTM D-1238. Four gram of uncompounded HDPE and compounded HDPE pellets from each formulation was prepared. It was then poured into a metallic cylinder bore which has been heated to 190°C. The melt formulation was extruded through a die by a weighted piston. The die is 8 mm in length, 2.095 mm in inner diameter and 9.5 mm in outer diameter. A weight was placed at the upper part of the piston to obtain a test load is 5 kilograms. The MFR was estimated as the weight in grams of the compounded HDPE extruded in 10 minutes.

4.4.3 Color Analysis

The color of the compounded HDPE was analyzed colorimetrically by using a Color Meter. During the test, the uncompound HDPE and the compounded HDPE were packed thoroughly in a petri dish. The excess amount of the sample was removed by using a smooth-surface glass. The measurement of color in the present experiment is an average of four measurements. "L", "a" and "b" can be used to calculate the Lightness corrected (L_c) from the relationship shown in Equation (4-1).

$$L_c = L - 13al - 3b \qquad (4\text{-}1)$$

The L_c value indicates the whiteness of the compounded samples. The higher the L_c value, the more whiteness the compounded resin possesses.