CHAPTER III

EXPERIMENTAL

3.1 Materials and Chemicals

Polymeric materials used were low density polyethylene (LDPE) J4324 supplied by Thai Petrochemical Industry Public Co, Ltd. (TPI), and linear low density polyethylene (LLDPE) L2020F supplied by Thai Polyethylene Co, Ltd. (TPE). Commercial specifications of those polymers are given in Table 3.1. Chemicals used were commercial grade dicumyl peroxide (melting point at 39°C, Akzo Chemical Co, Ltd.) as initiator, commercial grade tetrakis[methylene 3-(3',5'-di-t-butyl-4'-hydroxyl) propanoate] (Irganox 1010, melting point at 110-125°C, Ciba Geigy Co, Ltd.) as inhibitor. The analytical grade decahydronaphthalene or decalin (boiling point at 190°C, Carlo Erba Co, Ltd.) was used to determine the gel content of crosslinked polymer. All of the materials and chemicals were used as received.

Table 3.1 Specifications of LDPE J4324 and LLDPE L2020F.

Properties	Unit	J4324	L2020F
MFI $_{2.16/190°C}$	g/10min	2.3	2.0
Density	g/cm^3	0.921	0.920
Impact strength	g	160 [a]	80[b]
Tensile strength at yield	MPa	10.6	MD:9.8, TD: 8.8[b]
Tensile strength at break	MPa	12.0	MD:39.2,TD:30.4[b]
Elongation at break	%	640	MD:600, TD:810[b]
Tear stress Resistance	g/25 micron	-	MD:90, TD:280[b]

"a" Film thickness 40 micron.

"b" Film thickness 38 micron, MD : machine direction, TD : Transverse direction.

3.2 Instrument, Equipment and Glassware

Instruments used were DSC7 Perkin-Elmer differential scanning calorimeter (DSC), 1760X Perkin-Elmer Fourier-transform infra-red spectrophotometer (FTIR), PL-2000 Brabender Plastic-Corder with mixing chamber accessory, MPX 62.92 Gottfert melt flow indexer, and 150-C Waters gel permeation chromatography (GPC).

3.3 Characterization

3.3.1 Determination of Melting and Crystallization Temperature and Percentage of Crystallinity of LDPE and LLDPE

Melting temperature (T_m), crystallization temperature (T_c) and the percentage of crystallinity of LDPE and LLDPE were measured using DSC7 followed the method recommended by Perkin-Elmer [33]. For T_m measurement, temperature of scans were 50-250°C at the scanning rate of 10°C/min. The value of T_m was obtained from the second scan.

For T_c measurement, the individual polymer sample was heat up in a DSC furnace starting from 50 to 250°C at the scanning rate of 10°C/min in order to destroy its processing memory. Then it was cooled down to 50°C at the cooling rate of 10°C/min. Thus, T_c was obtained from the peak of exotherm. The percentage of crystallinity was determined directly from the ratio of the measured heat of fusion to the ideal heat of fusion of the perfect crystal of polyethylene of 68.4 cal/g [21].

3.3.2 Measurement of Melt Flow Index of LDPE and LLDPE

Melt flow indices of LDPE and LLDPE were measured using MPX 62.92 Gottfert followed DIN ISO1133 (the plunger with its rod which carries two circular reference markings at a distance of 30 mm from each other).

3.3.3 Measurement of Molecular Weight and Molecular Weight
Distribution of LDPE and LLDPE

Molecular weight of polymers was determined by GPC technique. The information on the number-, the weight-, and the Z-average molecular weight (M_n, M_w and M_z) which in this study only M_w was of interest. Molecular weight distribution (MWD) was also obtain in term of polydispersity index (M_w/M_n).

Approximately 0.034 g sample was dissolved in 20 mL o-dichlorobenzene (ODCB) at 135°C for overnight. The solution was then filtered through a micofilter and kept in a sample bottle, which was then introduced to the automatic injection device located in the instrument being control at 135°C. The 450 microlitres sample solution was automatically injected with the flowrate of 1.0 mL/min (ODCB as the eluent) into the injection port and subsequently passed through two high performance crosslinked polystyrene columns (trade name PLgel: Mixed -B) had the following specifications : column length 300 mm with the internal diameter of 7.5 mm, mixed bed column with the recommendation to size exclude of the molecular weight in the ranges of 500-10,000,000 g/mol). The different sizes of polymer excluded out of the columns were detected by a RI detector. The detector response against elution time or elution volume was detected on-line using a personnel computer with a software named Maxima 820 supplied by Waters. The experiments were repeated thrice and the average values were reported.

3.3.4 Determination of Short Chain Branching Concentration of LDPE
and LLDPE by FTIR

LDPE and LLDPE film (180-220 μ) were prepared using a hot press at 170°C with a force of 170 kN. The film was exposed to laser light in the FTIR sample compartment at the ambient. The number of scans was five with the resolution of 4 cm^{-1}, and the scanning wavenumber was from 4000 to 400 cm^{-1}. Determination of the short chain branch concentration per 1000 atoms of carbons was achieved followed the method described by Usami and Takayama [18].

3.4 Experimental : Studies of the Kinetics of Crosslinking Reaction of LDPE and LLDPE

The kinetics of crosslinking reaction of LDPE and LLDPE in the presence and in the absence of an inhibitor were studied using PL 2000 Brabender Plasti-Corder and DSC techniques. For the Plasticorder technique, the crosslinking reactions were subjected to mechanical shear force due to the contra-rotating of the twin screw during the crosslinking reaction, and this is called "the dynamic kinetics". For the DSC technique, no external force was applied to the polymer system therefore, it is called "the non-dynamic kinetics". Typical experimental procedure for both techniques used to study the kinetics of crosslinking reactions are given subsequently in Sections 3.4.1 and 3.4.2. The free radical generator was dicumyl peroxide and the inhibitor was tetrakis[methyl 3-(3′,5′-di-t-butyl-4′-hydroxyl)propanoate] (tradename Irganox 1010). The amount of initiator and inhibitor were varied according to Tables 3.2 and 3.3.

Table 3.2 Amount of DCP and Irganox 1010 for crosslinking reaction of LDPE and
LLDPE (35 g) by Rheometric technique.

Recipe No.	LDPE		Recipe No.	LLDPE	
	DCP (g)	Irganox (g)		DCP	Irganox (g)
1	-	-	15	-	-
2	0.07	-	16	0.07	-
3	0.14	-	17	0.14	-
4	0.28	-	18	0.21	-
5	0.32	-	19	0.28	-
6	0.42	-	20	0.35	-
7	0.56	-	21	0.42	-
8	0.70	-	22	0.42	0.035
10	0.86	-	23	0.42	0.070
11	0.70	0.035	24	0.42	0.14
12	0.70	0.070	25	0.42	0.21
13	0.70	0.14			
14	0.70	0.21			

Table 3.3 Amount of DCP and Irganox 1010 with a constant 35 g LDPE and LLDPE employed for the studies of the kinetics of crosslinking reactions using DSC technique.

Recipe No.	DCP (g)	Irganox (g)
1	0.28	-
2	0.42	-
3	0.56	-
4	0.70	-
5	0.70	0.035
6	0.70	0.07
7	0.70	0.14
8	0.70	0.21

3.4.1 Kinetics Study of Crosslinking Reaction Using PL 2000 Brabender Plasti-Corder

Prior to carrying out any new experiments, the torque-time was calibrated due to the compulsory of the software supplied by the supplier [34]. After the calibration, the preweighed 35 g LDPE or LLDPE was introduced first into the controlled-temperature mixing chamber set constantly for example at 165°C, the mixing screws were rotated at the speed of 50 rpm. The known amount of Irganox 1010 (if any) was subsequently introduced into the chamber. Then, a ram was put and fitted in the provided position of the chamber with a little bit of compression force until the polymer melted. The ram was then removed. When it was subjected to mechanical shear force in the chamber for a period of less than 6 min, its melt temperature raised up to about 173°C. After that time, the polymer melt temperature was maintain constant at 173°C. It should be noted that difference of the chamber and the polymer melt temperature was about 8°C or less dependent upon the initial temperature of the

chamber. After the polymer melt presented in the chamber for 6 minutes, the preweighed DCP was then introduced into the melt while the screw rotated continuously. The experiment terminated when the maximum torque was observed, which indicated that the crosslinking reaction was completed. Finally the crosslinked polymer was removed from the chamber which was subsequently clean up and was prepared for the next experiment. Each experiment was repeated for three times and only the average values were reported. The crosslinking reaction temperature were varied from 446 to 473 K.

Typical torque-time curve is given in Figure 3.1. The label a-b indicates polymer loading, b-c : polymer melting, c-d : crosslinking , and d-f : mechanical degradation of polymer.
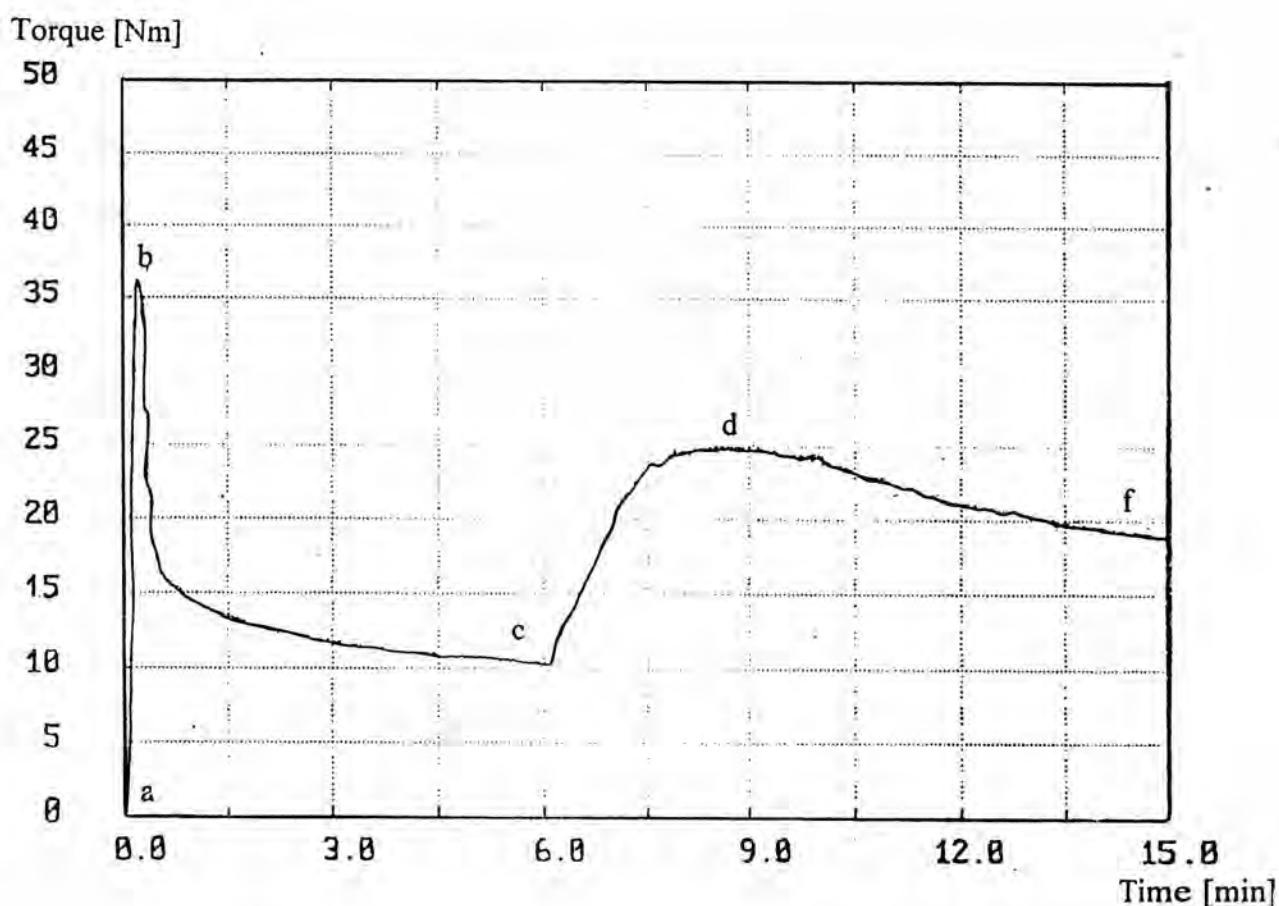
Figure 3.1 Typical torque-time curve ; DCP 0.8%w/w, rotor speed 50 rpm at temperature set point 165°C.

The variation of torque at the particular time can be used to calculate the crosslinking conversion according to Equation (3.1).

$$x = \frac{\Gamma_{max} - \Gamma_t}{\Gamma_{max} - \Gamma_{min}} \qquad (3.1)$$

where x is the conversion, Γ_{max}(Nm) and Γ_{min}(Nm) are maximum and minimum torques, respectively, and Γ_t (Nm) the torque at a given time.

3.4.2 Kinetics Study of Crosslinking Reaction Using Differential Scanning Calorimeter

LDPE or LLDPE was first compounded with DCP and/or Irganox 1010 prior to carrying out the DSC experiments. Generally, 35.00 g LDPE or LLDPE was mixed with the preweighed DCP and/or inhibitor for 2-3 minutes in the mixing chamber of Brabender at 120°C for LDPE, at 125°C for LLDPE. Subsequently the compounded polymer was allowed to cool down to room temperature. The sample was subsequently stored in darkness at 18°C prior to the use for further study.

Typically 15-20 mg compounded LDPE or LLDPE was preweighed in an aluminium pan. The temperature scanning experiment (a heating rate of 10°C/min) from 50 to 250°C provided the value of total heat of reaction (ΔH_s). The isothermal reaction was also carried out for a specified period of time. Then the compounded sample was immediately heated up from that temperature upto 250°C using the temperature scanning mode with a heating rate of 10°C/min to obtain the residual heat of reaction (ΔH_{res}). The experiments were repeated two times and only the average values were reported. The crosslinking reaction temperature were varied from 393 to 423 K.

The average values of ΔH_s and ΔH_{res} of each compound were used for the determination of crosslink conversion (x) by Equation (3.2).

$$x = \frac{\Delta H_s - \Delta H_{res}}{\Delta H_s} \qquad (3.2)$$

3.5 Preparation of Crosslinked LDPE or LLDPE Sample

The compounded LDPE or LLDPE by Brabender Plasticorder were crosslinked at 180°C for 15 minutes in a hot press with the force of 170 kN. Then the crosslinked samples were cooled down to room temperature using trap water. The sample size was in the dimension of 10 x 10 cm^2 and 2 mm thickness.

3.5.1 Determination of Gel Content of the Crosslinked LDPE or LLDPE

Gel content of the crosslinked LDPE or LLDPE was determined according to ASTM D2765. Decalin was used as the solvent.

3.5.2 Determination of T_m, T_c and Percentage of Crystallinity of Crosslinked LDPE and LLDPE

The compounded LDPE or LLDPE was crosslinked in an aluminum pan of the DSC furnace. The operation condition was the temperature scanning range of 50 to 250°C with the scanning rate of 10°C/min. T_m and T_c of the crosslinked polymer was subsequently measured thereafter the completion of the crosslinking reaction. It was cooled down to 50°C with the cooling rate of 10°C/min to obtain the value of T_c from the peak of the exotherm. Then it was reheated again from 50 to 250°C with the scanning rate 10°C/min to obtain the value of T_m from the peak of the endotherm. The values of percentage of crystallinity were calculated using the same procedure mentioned in Section 3.3.1.