CHAPTER III
EXPERIMENTAL SECTION

3.1 Materials

The materials used in the present studied are as following:

1. Linear Low Density Polyethylene (LLDPE)

The LLDPE used in this work was blown-film grade (L1810F) supplied by Thai Polyethylene Company. The material was in pellet form and was used as a polymer matrix. The chemical structure and the physical properties of LLDPE are shown in a Figure 3.1 and Table 3.1, respectively.
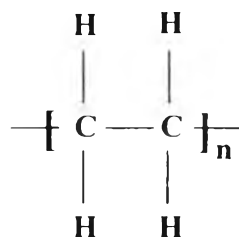
$$\left[\begin{array}{cc} \overset{\displaystyle H}{\underset{\displaystyle H}{|}} & \overset{\displaystyle H}{\underset{\displaystyle H}{|}} \\ C & -C \end{array}\right]_n$$

Figure 3.1 Chemical structure of LLDPE.

Table 3.1 Physical properties of LLDPE.

Properties	LLDPE
MFI[A] (g/10min)	1
Melt density[B] (g/cm^3)	0.718
M_W[C], (g/mol)	84460
M_n[D], (g/mol)	3481
MWD[E]	24.3
Melting temperature (°C)	135

Note: A, B: given from supplier

C, D, and E: characterized by GPC

2. Natural Rubber (STR5L)

This rubber was purchased from Rayong Bangkok Rubber Co., Ltd. The melt density of NR was given from the supplier as 0.700 g/cm^3. The chemical structure and physical properties of NR are shown in Figure 3.2 and Table 3.2, respectively.
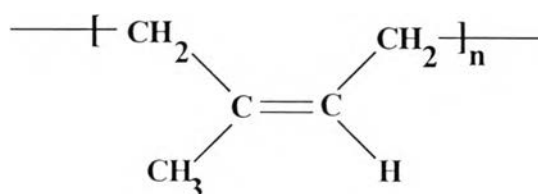

Figure 3.2 Chemical structure of cis-1,4-polyisoprene.

Table 3.2 Specification for Standard Thai Rubber (STR 5L).

Specification	Specification limit
Dirt (%wt)	0.04
Ash (%wt)	0.40
Nitrogen (%wt)	0.60
Volatile matter (%wt)	0.80
Initial plasticity (P_0) (min)	35
Plasticity Retention Index (PRI) (%)	60
Color Limit (Lovibond Scale)	6.0

3. Maleic Anhydride (MA)

The laboratory grade maleic anhydride (MA), used as a compatibilizer, was purchased from Fluka. The material is a briquette or white fused mass, complete and clear solubility in water (4g/10ml water). A chemical structure and physical properties are shown in Figure 3.3 and Table 3.3, respectively.
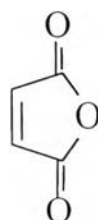

Figure 3.3 Chemical structure of MA.

Table 3.3 Physical Properties of MA.

Properties	Value
Formula	$C_4H_2O_3$
Formula weight, (g/mol)	98.06
m.p., (°C)	52.85
b.p., (°C)	202
Bulk density, (g/cm³)	1.48
Melt density, (g/cm³)	1.30

4. Toluene

The analytical grade toluene used as a solvent for extracting NR for the morphological study was purchased from J.T. Baker. The physical properties of toluene are shown in Table 3.4.

Table 3.4 Properties of toluene.

Properties	Value
Formula	C_7H_8
Formula weight, (g/mol)	92.14
b.p., (°C)	110.75
m.p., (°C)	-94.85

5. Tetrahydrofuran (THF)

The HPLC grade THF supplied by J.T. Baker was used as a solvent for GPC Waters 600E at room temperature.

6. Dichrolobenzene

The HPLC grade dichlorobenzene supplied by Lab Scan Co., Ltd. was used as a solvent for GPC Waters 150-c at 140 °C.

3.2 Methodology

3.2.1 Blend preparation

3.2.1.1 Mastication of Natural Rubber (NR)

Natural rubber was masticated using a two-roll mill (Lab Tech, LMR 110) the temperature of the front roll and the back roll were 20°C and 30°C, respectively. Three samples of NR with different molecular weight were prepared by varying mastication time, as shown in Table 3.5. For convenience, these natural rubbers are designed as NR_5, NR_{10} and NR_{25} to indicate the mastication times of 5, 10, and 25 min, respectively. It has to note that NR_{10} was not obtained from the same source as that of NR_5 and NR_{25}.

Table 3.5 Characterization of molecular weight of natural rubber.

Characterization	NR_5	NR_{10}	NR_{25}
M_w, (g/mol)	781,222	125,000	429,772
M_n	162,307	22,242	119,477
MWD	4.81	5.63	3.60
Masticated time, (min)	5	10	25

A 400 g of NR was mill at roller speed of 16 rpm. The gap between the rolls was adjustable within a range of 5-10 mm and kneading the rubber was kneaded by multiple passes through the gap before removal from the mill.

3.2.1.2 Preparation of grafted NR with MA

A certain amount of masticated NR of each composition, as shown in following Flow chart I was milled in the two-roll mill for 3 min. The temperature of the front roll and the back roll were 170 °C and 160 °C, respectively with the roller speed of 16 rpm. Maleic anhydride was added into the masticated NR at 3 min and further mixed for 5 min. The gap between the rolls was adjustable within a range of 5-10 mm and the sample was kneaded by multiple passes through the gap and then removed from the mill. The grafted NR with MA was kept in a desiccator.

Flow chart I diagram of preparation of grafted NR with MA.

| Masticated NR | $\xrightarrow{\text{3 min}}$ | Adding MA | $\xrightarrow{\text{5 min}}$ | NR-g-MA |

On two-roll mill, T = 170 °C
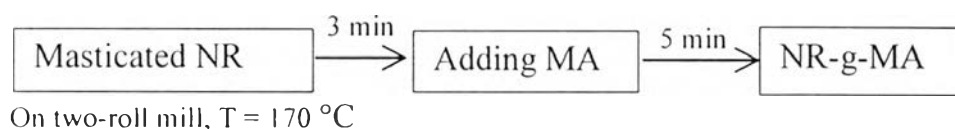
3.2.1.3 Preparation of blending of LLDPE/NR with MA

A certain amount of LLDPE of each composition was melt by using the two-roll mill for 3 min. Maleic anhydride was added in the melt LLDPE at 3 min and further mixed for 5 min as shown in Flow chart II. The temperature of the front roll and the back roll were 170 °C and 160 °C respectively with the roller speed of 16 rpm. Then the masticated rubber was added into the grafted LLDPE with MA at 5 min and further mixed for 5 min. The gap between the rolls was adjustable within a range of 5-10 mm and the sample was kneaded by multiple passes through the gap and then removed from the mill. The blends were shredded into small pieces by shredder machine and further put into the Collin co-rotating twin-screw kneader ZK-25 (25x30D) to completely mixed. Temperatures setting were shown in Figure 3.4. After passing through a water bath, the melt was solidified and cut into pellet form in a pelletizer.
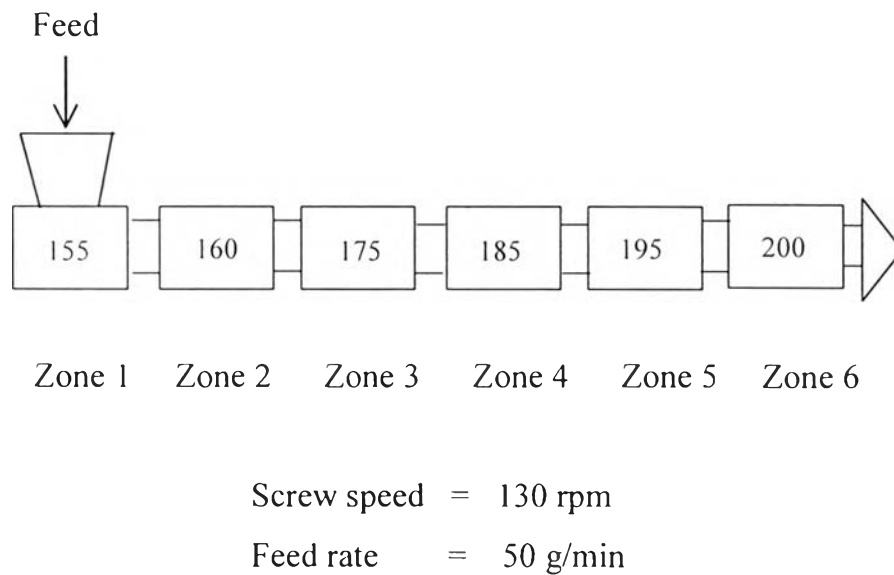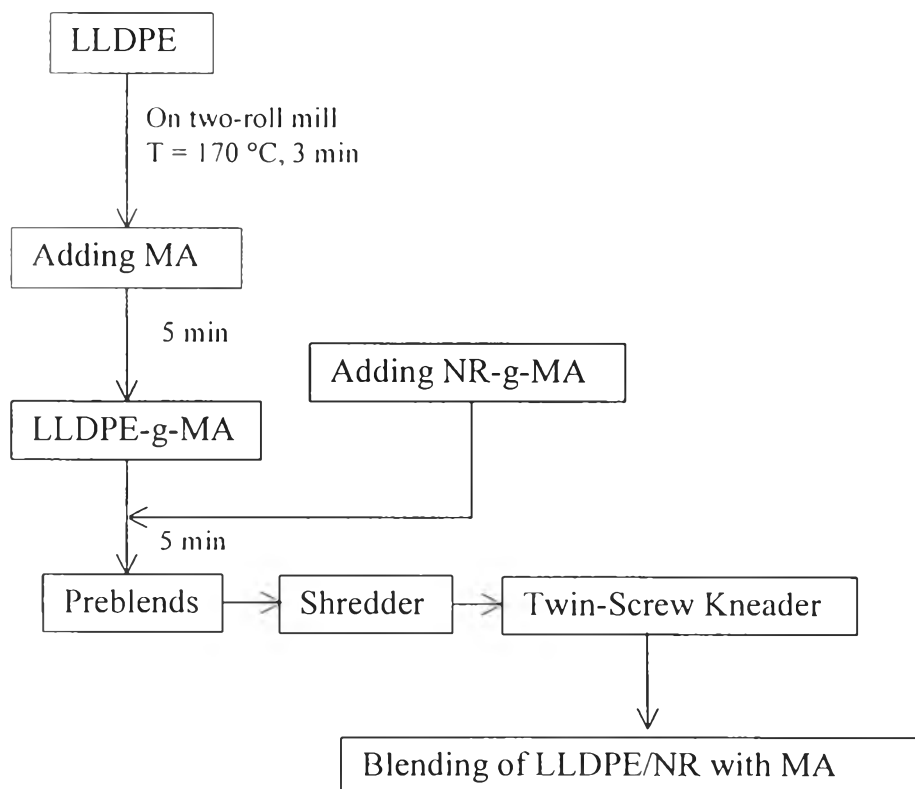
Zone 1   Zone 2   Zone 3   Zone 4   Zone 5   Zone 6

Screw speed   =   130 rpm

Feed rate   =   50 g/min

Figure 3.4 Condition of the twin-screw kneader.

Flow chart II diagram of preparation of blending of LLDPE/NR with MA.

3.2.1.4 Preparation of blending of LLDPE/NR without MA

First, LLDPE was melt on two roll mill at 170 °C for 5 min. The masticated NR was added into melt LLDPE after 5 min and further mixed for 5 min on the two-roll mill. The amount of each material was added as following the Flow chart III. The temperature of the front roll and the back roll were 170 °C and 160 °C respectively with the roller speed of 16 rpm. The gap between the rolls was adjustable within a range of 5-10 mm and the sample was kneaded by multiple passes through the gap and then removed from the mill. The blends were shredded into small pieces by shredder machine and further put into the twin-screw kneader to complete mixing.

Flow chart III diagram of preparation of blending of LLDPE/NR without MA.
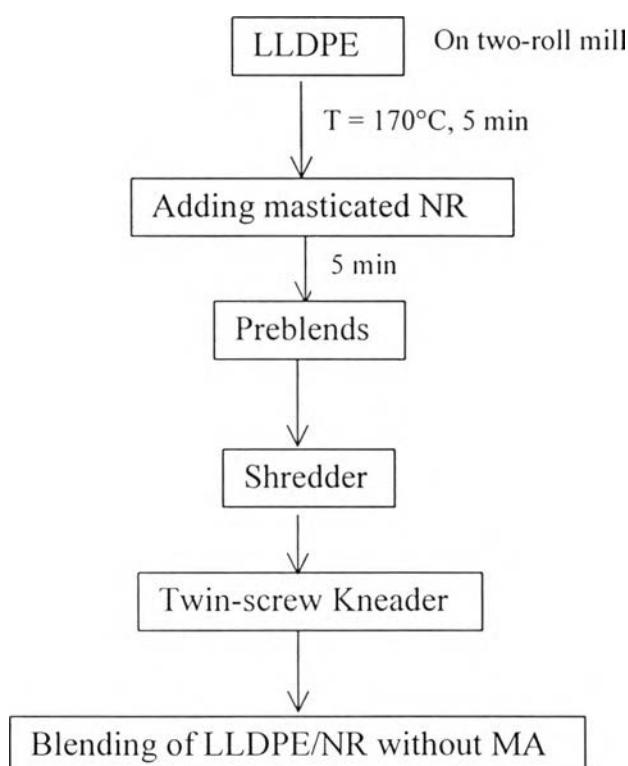
3.2.2 Determination of % grafting of MA onto LLDPE and NR

Analysis of the modified by MA polymer was done by infrared (IR) spectroscopy using pressed films of the produced polymer. A grafted LLDPE and NR with MA were expected from the preparation step of blending of LLDPE/NR with MA and grafted NR with MA, respectively. These samples were separated into two parts to studying the % grafting of MA onto LLDPE and NR.

3.2.2.1 Sample preparation for removal of unreacted MA

3.2.2.1.1 Graft of LLDPE with MA

The crude polymer was purified by precipitation from hot dichlorobenzene solution by addition to acetone. The hot solutions of polymer were filtered through cheesecloth. Then the sample was dried in vacuum oven at the temperature of 110 °C for 24 hr. The certain amount of the sample was pressed between two plates on a compression molding. The temperature and pressure were 170 °C and 15 tons for 10 min without mold. Then the sample was cooled under pressure to room temperature. Finally the thin film of LLDPE-g-MA was obtained.

3.2.2.1.2 Graft of NR with MA

The crude polymer was immersed in hot water for 12 hr and dried in vacuum oven at temperature of 60 °C for 12 hr. The certain amount of the sample was pressed between two plates on a compression molding. The temperature and pressure were 170 °C and 15 tons for 10 min without mold. Then the sample was cooled under pressure to room temperature. Finally the thin film of NR-g-MA was obtained.

3.2.2.2 Sample preparation without removal of unreacted MA

The certain amount of the sample was pressed between two plates on a compression molding. The temperature and pressure were 170 °C and 15 tons for 10 min without mold. Then the sample was cooled under pressure to room temperature. Finally the thin film of sample was obtained.

3.2.3 Molding

62 g of the sample in the form of granules was pressed on a Wabash V50H compression press. The steps used in this process for this study were 170 °C without pressure for 5 min, 170 °C with 5 tons forces for 5 min, and 170 °C with 15 tons forces for 5 min. Molds were cooled under pressure to room temperature. The mold used was a picture-frame type mode stainless steel coated with chromium. Thickness of the mold cavity was about 3 mm.

3.2.4 Melt Flow Index (MFI)

A sample weighting 5 g was placed into the barrel on the top of the instrument. The die diameter was 1.180 mm and the die length was 8 mm. Melt flow index (MFI) of the samples were determined following ASTM D1238 on a Zwick 4105 Extrusion Plastometer with piston load weight of 2.16 kg at 190 °C for all samples. An average was taken for three measurements.

3.2.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry was carried out on a NETZSCH DSC-200.

Principle

Structure changes are usually associated with changes in heat absorption or emissions. Scanning calorimetry can measure changes at constant heating or cooling rates. The differences in heat loss or gain between the sample and the reference cells are measured in a differential scanning

calorimeter. In this case the heat input needed to maintain both cells at the same temperature is measured. The configuration of this technique is schematically drawn in Figure 3.5.
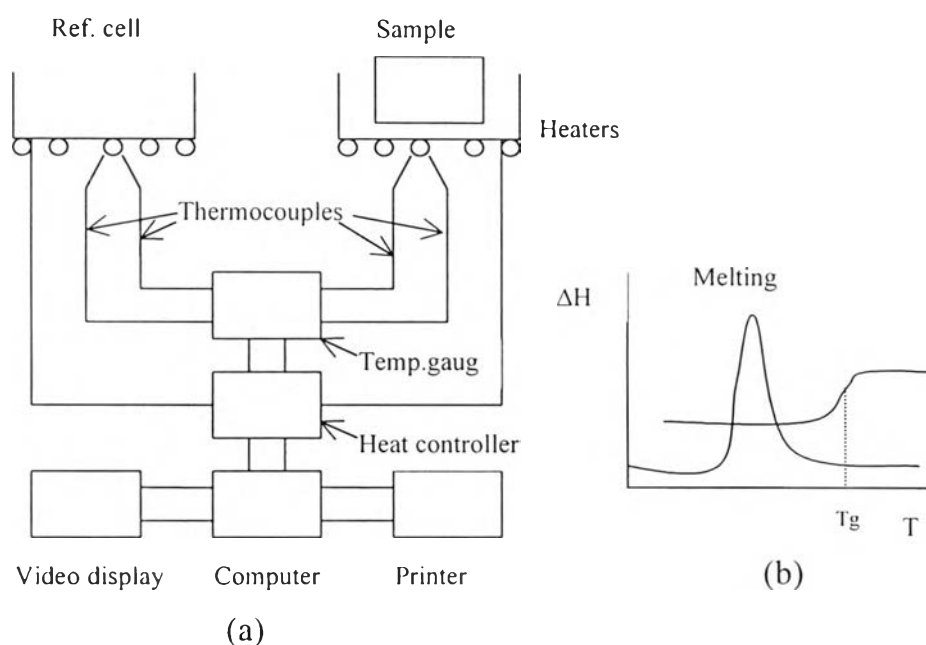

Figure 3.5 Schematic of DSC: (a) configuration of DSC technique; (b)thermogram obtained from DSC.

The cells are mounted in a metal block which can be cooled for more efficient heat stability. The thermocouples measure the temperature as well as differences in the temperature. The heat controller quickly compensates the difference of energy consumption and the amount of compensation is measured.

Procedure

The thermal behaviors of the LLDPE/NR blends samples were determined on a NETZSCH DSC-200. Sample of 5-7 mg was sealed in clamped aluminum sample pans. The temperature was programmed at 10° C/min in all cases. Liquid Nitrogen Cooling Accessory was used as a coolant

system. After loading the sample into the instrument chamber, the chamber was purged with dry nitrogen. The heating and cooling program are following;

The sample was heated from 30 °C to 150 °C and cooled down to 30 °C to determined melting temperature(T_m), crystallization temperature (T_c) and enthalpy of fusion (ΔH_f). T_g was determined by cooled down the samples from 30 °C to –120 °C and heated up to 30 °C. The T_g of the sample was taken as the temperature corresponding to 50% of the transition, as indicated in Figure 3.5(b).

The melting temperature, crystallization temperature, grass transition temperature, and heat of fusion of samples were determined from the thermograms. For estimation of the degree of crystallinity, the polymer was presumed to be composed of distinct, non-interacting amorphous and crystalline regions where reordering of the polymer structure only occurred at the melting temperature of the crystalline component. The crystallinity (X_c) is calculated using

$$X_c = \Delta H / \Delta H_{100} \qquad (3.1)$$

where ΔH and ΔH_{100} are the measured enthalpy of melting of the sample and the enthalpy of melting of a 100% pure crystalline of the same polymer, respectively.

3.2.6 Scanning Electron Microscope (SEM)

Morphologies were studied using a SEM, JEOL 5200-2AE (MP152001) with a magnification range of 35-200,000 times. Micrographs of the fracture surface were made using a voltage of 15-25 kV.

Principle

The principle of a scanning electron microscope (Figure 3.6) is as follows. An electron gun and a set of a heated tungsten filament, an anode attracting the emitted electrons and a focusing electrode (gun bias), form a small electron probe. The important parameter of the gun is its brightness that is given by the total number of electrons coming from a unit area of the source into a unit solid angle. In order to increase the brightness, it is possible to increase the emission current by replacing tungsten with lanthanum hexaborite. Alternatively, the area of the source can be reduced with a point filament or the emission angle can be reduced by field emission.
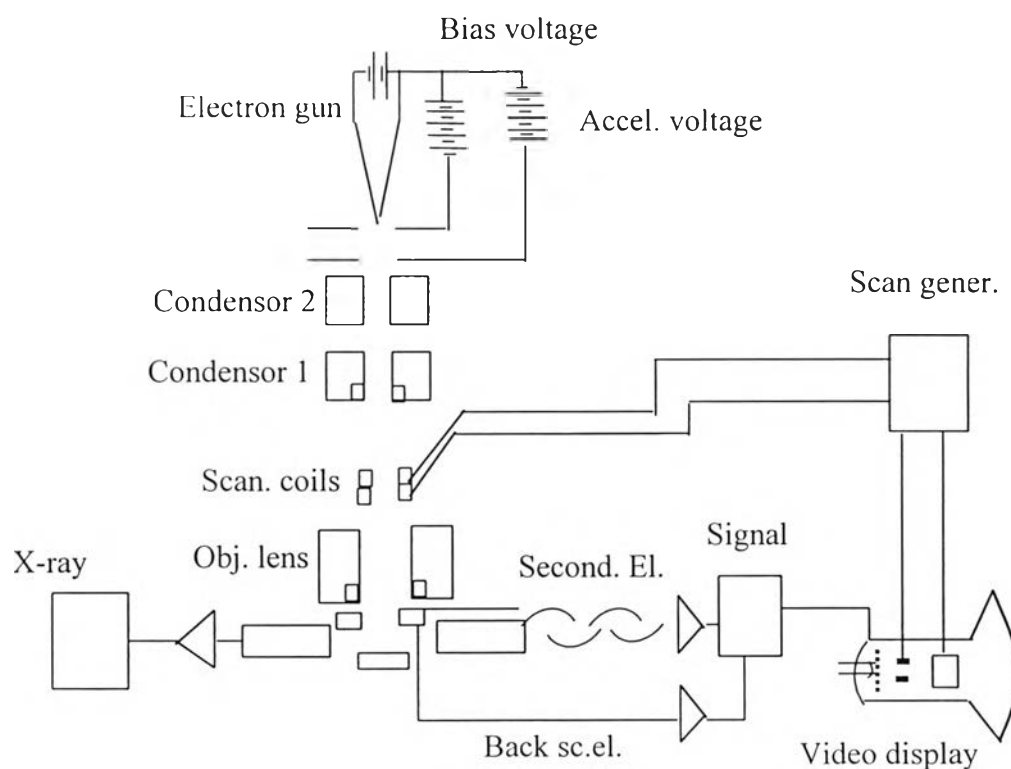
Figure 3.6 Schematic diagram of a scanning electron microscope.

The probe size is reduced by demagnification of the filament image using two electromagnetic lenses and then focusing onto the specimen surface by using a final (or objective) lens. The probe is scanned on the specimen by two set of scanning coils controlled by the same generator while the cathode ray tube used to observe the image. The signal is detected by a low noise scintillator-photomultiplier-amplifier system which is also used to modulates the display signal. Each point of the scanned raster on the sample thus has a corresponding point on the display screen. Once the probe is focused and corrected for astigmatism, changing the size of the scanned area without focusing can change the magnification (Folkes and Hope, 1993).

Procedure

Samples were taken from cryogenically (in liquid nitrogen) fractured surface of compression mould tensile specimens. The sample was treated with for two days to extract the NR phase, followed by drying in an oven at 110°C for 1 day. Surfaces were sputtered with gold before viewing.

3.2.7 Instron Universal Testing Machine

The mechanical testing samples were obtained from the compression-molded sheet by using a Wabash V 50 H compression molder. The tensile properties were measured by using an Instron Universal Testing Machine, Model 4206, according to the ASTM D638-91 test procedure in the extension mode. The load cell of 100 kN and 500 mm/min crosshead speed were carried out for all test specimens. The dumbell shape specimens were die cut from sheets into type IV, for specimen dimensions, the width of narrow section was 6 mm and the gage length was 25 mm as in Figure 3.7 and Table 3.6. Five specimens were tested for each sample.
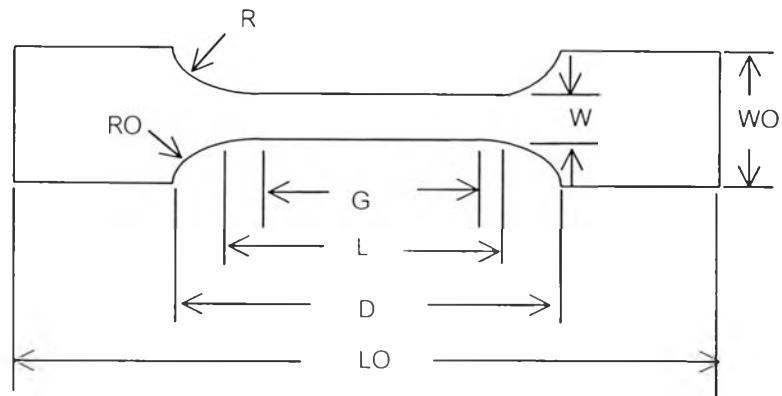
Figure 3.7 Dimension of tensile testing specimen.

Table 3.6 Dimension of tensile testing specimen as shown in Figure 3.7.

Definition	Dimensions (mm)
W-Width of narrow section	6
L-Length of narrow section	33
WO-Width of overall	25
LO-Length overall	115
G-Guage length	25
D-Distance between grips	80
R-Radius of fillet	14
RO-Outer radius	25

The tensile modulus using in this thesis is manual Young's modulus, that is the steepest linear region at the start of the testing curve and ends it at the yield point. It can be defined by dividing the corresponding stress by the designed strain.

The percent elongation at break is the extension (change in guage length) at break. It can be calculated by dividing the extension by original guage length and multiplied by 100.

The tensile strength at break is maximum tensile stress at break point sustained by specimen during a tension test. It can be calculated by dividing the maximum load at break point by original area.

The yield strength is the stress at which a material exhibits a specified limiting deviation from the proportionality of stress to strain. Unless otherwise specified, this stress will be at the yield point.

3.2.8 Fourier Transform Infrared (FT-IR)

The percent grafting of MA onto LLDPE and NR were determined by measuring the level of carbonyl (1713 cm^{-1}) absorbances using a Bruker FT-IR spectrometer with 64 scans at a resolution of 4 cm^{-1}. A frequency range of 4,000-400 cm^{-1} was observed using a deuterated triglucinesulfate detector (DTGS) with a specific detectivity, D*, of 1×10^9 cmHz$^{1/2}$W^{-1}. The thickness of each piece of film was measured to 0.08 ± 0.007 mm with a micrometer gauge. Sample films, free form wrinkles, were mounted on standard FT-IR sample plates using a removable magnetic cover or removable tape.

3.2.9 Gel Permeation Chromatography (GPC)

A room temperature gel permeation chromatography (GPC) was carried out on waters 600E instrument to determine the molecular weight of natural rubber. A solvent used in this study was tetrahydrofuran (THF). Characteristics of the column HT4 were calibrated using narrow MWD polystyrene standard. The operating condition of temperature, flow rate, and injection volume were 35 °C, 1 cm^3/min, and 60 μL, respectively.
For determination of M$_W$, M$_n$, and MWD of LLDPE and LLDPE/NR blends were determined by using gel permeation chromatography (GPC) with Water 150 C ALC/GPC instruments. A solvent used in this studied was dichrorobenzene. The operating conditions of temperature and flow rate were 135 °C and 1 cm^3/min, respectively. There were three columns of instrument

consist of μ-styragel 10^4, 10^5, and 10^6. Preparation of the calibration curve was described in Appendix A.

3.2.10 Vicat Softening Temperature (VST, Model CEAST 6505)

The vicat softening temperature testing specimens were obtained from the compression-molded sheet by using a Wabash V 50 H compression molder. The vicat softening temperature was determined by using VST, CEAST 6505, according to ASTM D1525 test procedure. The specimen and needle are heated at the rate of 120 °C/h with the load of 1 kg. Used at least two specimens to test each sample. The specimen is flat and a minimum width of 12 mm and a minimum thickness of 3 mm. It is support on the flat, solid base during the test.