

Chapter III

EXPERIMENTAL



3.1 Materials.

3.1.1 Low density polyethylene (LDPE)

There are two types of low density polyethylene resin used as:

1) JJ4324 a product of IRPC Public Company Limited, having an molecular weight average of 240 kg/mol and a density of 921 kg/m³ (hereafter called LDPE240KD) and MFI of 5.5 g/10min. Melting temperature is 110-120°C.

2) LD1905F a product of Thai Polyethylene Public Company limited (TPE), having an average molecular weight of 125 kg/mol and a density of 919 kg/m³ (hereafter called LDPE125KD) and MFI of 5.0 g/10 min. Melting temperature is 110-120°C.

3.1.2 Poly(lactic acid) (PLA)

Poly(lactic acid) resin used is 4042D, a product of Nature Work Company Limited, having melt flow index of 1.4-5 g/10 min and a density of 1240 kg/m³ (hereafter called PLA). An average molecular weight is 74 kg/mol, melt temperature is 210 ± 8 °C.

3.1.3 Low density polyethylene graft maleic anhydride (LLDPE-g-MA)

Linear low density polyethylene graft maleic anhydride used is FusaBond[®] E MX110D, a product of DuPont, having a an average melt flow index of 25 g/10 min (16 g/10min to 34 g/10min) and density of 925 kg/m³. Melting point is 122 °C.

3.1.4 Proteinase K

Proteinase K from Tritirachium album in a lyophilized powder, from Sigma-Aldrich, has an enzymatic activity of not less than 30 units/mg protein. Recommended working pH is 7.5.

3.1.5 Sodium Azide (NaN_3)

Sodium azide S2002, grade of ReagentPlus[®], was supplied by Sigma-Aldrich with purity 99.5% in a powder stage. Molecular weight is 65.01 g/mole.

3.1.6 TRIS hydrochloride buffer

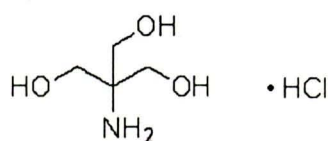


Figure 3.1 Chemical structure of TRIS hydrochloride buffer

Tris(hydroxymethyl)aminomethane hydrochloride, ($\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3 \cdot \text{HCl}$), that show chemical structure in Figure 3.1. It was supplied from Sigma-Aldrich in a powder stage with purity >99%. Molecular weight is 157.6 g/mole.

3.2 Instruments and Apparatus

Instruments and apparatus used for this research are as follows:

1. Twin screw extruder (Model PL2100, Brabender Plasti-Corder, German).
2. Injection Machine (Model CLF-80T, Chuan Lih Fa, China)
3. Crusher (Model 881203, Brabender, German)
4. Dryer hopper (Model SHD-25, SHD, China)
5. Universal testing machine (Model 5565, Instron, USA)
6. Pendulum impact testing machine (Model BPI, Atlas, England)
7. Scanning Electron Microscope (Model JSM6400, JEOL, Japan)
8. Differential Scanning Calorimeter (Model DSC-7, Perkin Elmer, USA)
9. Thermogravimetric Analyzer (Model SDT2960, TA, USA)
10. Incubator Shaker (Model Innova[®]40, New Brunswick Scientific, USA)
11. Weighing Machine (Model Analytical plus, OHAUS, USA)

12. Vacuum oven (Model J-DV01, JISIO, Japan)

13. Melt Flow Indexer (Model 4004, Keyence, Canada)

3.3 Blends preparation

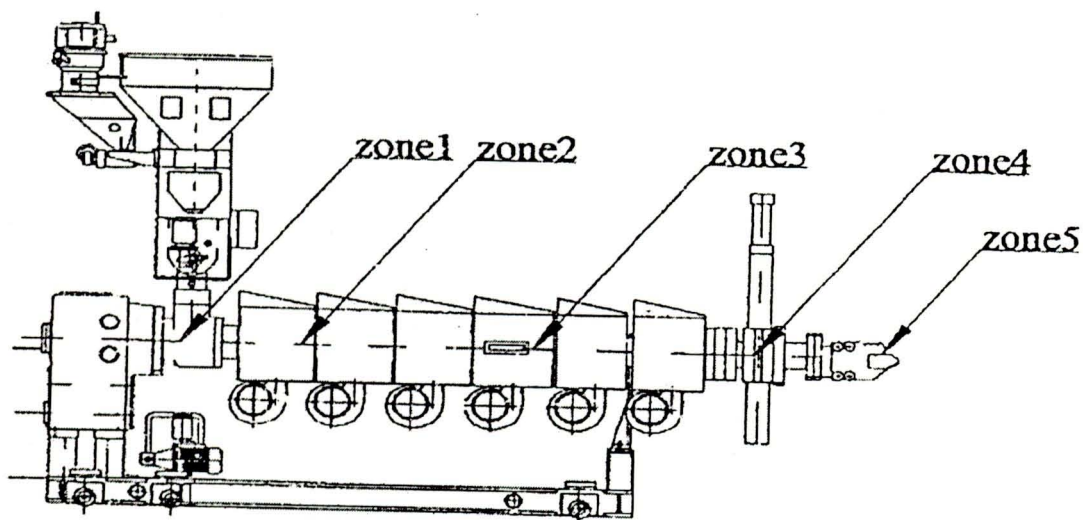
The blends were prepared in a twin screw Brabender extruder model 42/7 (D=42 mm, L/D=7) attached to a Brabender Plasti-Corder PL2100. The twin screw extruder is an intermeshing counter-rotating twin screw extruder and processing temperature setting is showed in Figure 3.2. The weight ratios of LDPE and PLA were 80/20, 90/10 and 95/5. The compatibilizer concentrations used were 1 and 3 pphr for each LDPE/PLA weight ratio. The various blend compositions prepared are given in Table 3.1.

Table 3.1: Formulation of LDPE/PLA mixes (% by weight)

Formulation Name	LDPE240KD	LDPE125KD	PLA	LLDPE-g-MA(pphr)
LDPE240KD/80	80	0	20	0
LDPE240KD/90	90	0	10	0
LDPE240KD/95	95	0	5	0
LDPE240KD/80:1	80	0	20	1
LDPE240KD/80:3	80	0	20	3
LDPE240KD/95:1	95	0	5	1
LDPE240KD/95:3	95	0	5	3
LDPE125KD/80	0	80	20	0
LDPE125KD/90	0	90	10	0
LDPE125KD/95	0	95	5	0
LDPE125KD/80:1	0	80	20	1
LDPE125KD/80:3	0	80	20	3
LDPE125KD/95:1	0	95	5	1
LDPE125KD/95:3	0	95	5	3

All materials for each blend were hand tumbled in a mixing bowl for 10 minutes. The mixed materials were then introduced into a vacuum oven at 80 °C for 4

hrs, with the controlled temperatures at all four zones and die zone at 190 °C; the speed was fixed at 40 rpm. The long strand extrudates were cooled at room temperature and chopped into granules using the pelletizer and subsequently dried at 80 °C for 3 hrs and then keep in vacuum oven at room temperature before other testings.



Zone 1: Temperature of feed zone	= 190 °C
Zone 2: Temperature of compression zone	= 210 °C
Zone 3: Temperature of metering zone	= 200 °C
Zone 4: Temperature of screen changer	= 200 °C
Zone 5: Temperature of die	= 185 °C

Figure 3.2 Twin screw extruder for blending

3.4 Rheological properties by melt flow index

The melt flow index was measured according to ASTM D1238 using the Keyence model 4004. The weight in gram of molten resin through an orifice for 10 minutes under a weight of 2.16 kg at temperature of 190 °C.

3.5 Thermal analysis

3.5.1 DSC analysis

The melting and glass transition temperatures of the blend were studied using DSC-7 under a nitrogen atmosphere with a heating and cooling rate of 10 °C/min. The temperature cycle consisted of an initial heating from 25°C to 180°C and annealed for 5 min to remove the thermal history. The cooling scan was then begun by cooling the sample to 25°C at a cooling rate of 10°C/min. Finally, the second heating scan was done by heating the sample from 25°C to 180°C again at a heating rate of 10°C/min. Data were collected during the second heating thermogram. DSC feature is showed in Figure 3.3.

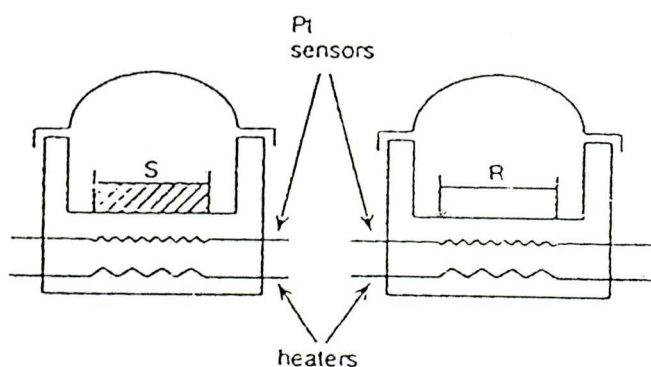


Figure 3.3 Typical DSC cells showing the sample (S) and reference (R)

3.5.2 TGA analysis

Thermal analysis was determined using SDT 2960 that measured the change in weight of materials with increasing temperature. The TGA data of the blends were obtained by heating the samples under a nitrogen atmosphere at a heating rate of 20°C/min to the final temperature of 580 °C.

3.6 Morphological observation

The SEM samples for morphology studies were directly taken from the broken pieces in a nitrogen atmosphere. Surface morphology of the fractured surface of the blends were examined using JSM6400 at 10keV. The samples were coated with gold

before analysis. Then the degraded samples were examined on its sheet surface after the enzyme degradation.

3.7 Mechanical properties

3.7.1 Izod impact strength testing

Izod impact testing machine show in Figure 3.4. The testing specimens of 64 mm x 12.7 mm x 3.2 mm for the measurement of Izod impact strength were prepared by following ASTM D4101 using the BPI testing machine with a load of 5.4 J according to the standard method of ASTM D256, a pendulum swung on its track and struck a notched, cantilevered plastic sample. The energy lost (required to break the sample) as the pendulum continued on its path was measured from the distance of its following through.

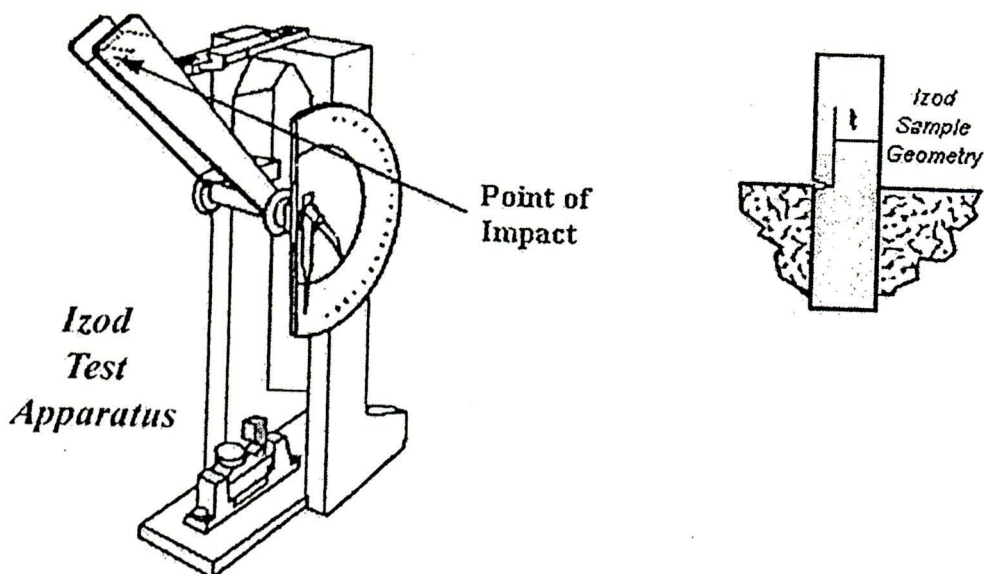
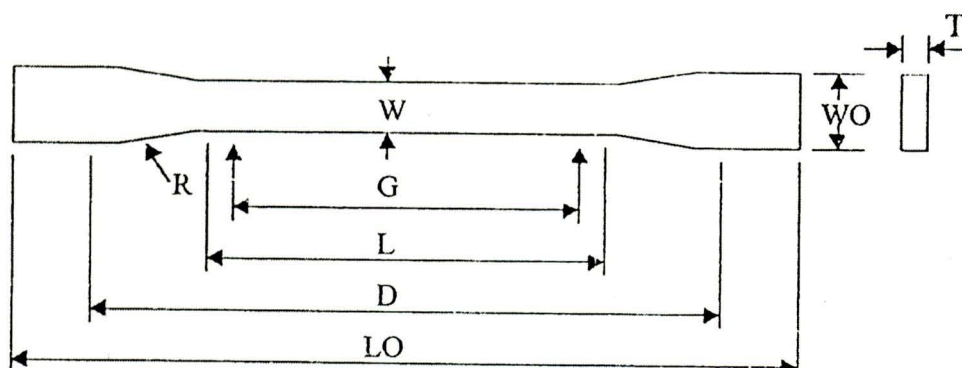


Figure 3.4 Izod impact strength apparatus and test specimen.

3.7.2 Tensile property measurement

The dumbbell specimens for the tensile property measurement were prepared according to ASTM D4101. The universal testing machine was used in accordance with ASTM D638. The sample was pulled, by the tensile testing machine with a load cell of 5 kN, from both ends with a load cell of 5 kN, a crosshead speed of 500 mm/min, and a gauge length of 115 mm as shown in Figure 3.5. The force required to pull the specimen apart, the length of sample after stretching, were measured.



W :	Width of narrow section	13
L :	Length of narrow section	57
WO :	Width overall	19
LO :	Length overall	165
G :	Gauge length	50
D :	Distance between grips	115
R :	Radius of fillet	76
T :	Thickness	3.2

All dimension in millimeters (mm)

Figure 3.5 Tensile testing apparatus and test specimen

3.8 Enzyme degradation observation

For enzymatic degradation studies, each specimen (10 mm x 10 mm x 0.6 mm) was placed in a vial filled with 10 ml of Tris HCl buffer solution (pH=8.6) containing 2.0 mg proteinase K and 2.0 mg sodium azide. The vials were allowed to shake at 100 rpm in a shaker thermostated at 37 °C. The buffered enzyme system was changed every 12 hours for 4 days and then every 24 hours for 2 days to, totally 144 hours to restored the original level of enzymatic activity. For a given experiment, three replicate samples were withdrawn from the degradation medium, and washed with distilled water. After the specimens were vacuum dried at room temperature for 1 week. Then sample were investigated for their appearance by SEM and weight loss by weighing.