

CHAPTER III

EXPERIMENTAL

3.1 Materials

The materials used in this thesis were commercial grade. The commercial injection grade high-density polyethylene (HDPE) Polene R1760 (MFI_{2,16 kg, 463 K} = 9.0 g/10 min) and the high impact acrylonitrile-butadiene-styrene (ABS) Polene GA850 (MFI_{5 kg, 473 K} = 18.0 g/10 min) were supplied by IRPC Public Company Limited, Rayong, Thailand. Maleic anhydride (MAH) and dicumyl peroxide (DCP 98%) were purchased from Aldrich, Germany.

3.2 Apparatus and experiments

Followings are the list of major instruments used in this research

1. LTE26-40 Co-rotating intermeshing twin-screw Lab Tech Engineering twin screw extruder, Thailand, having a screw diameter, D of 26 mm with an L/D ratio = 40, with a rotational speed of 40 rpm.
2. Differential Scanning Calorimeter DSC-200 NETZSCH, Germany
3. Capillary Rheometer RH-7 Rosand Single Bore, United Kingdom
4. Scanning Electron Microscope JSM-5800 LV JEOL , Japan
5. Fourier Transform Infrared spectrometer Bruker Tensor 27, Germany

6. Injection molding machine Toshiba IS100G 100MT, Japan
7. Universal testing machine Lloyd LR10K, USA
8. Pendulum impact tester 258D, USA
9. Xenon Weather meter, Suga, Japan with the following condition:
 - Irradiance $25\sim 70\text{W/m}^2$ (300~400nm) in range optionally selection setting and automatic operation adjustment.
 - Wave length 340 nm.
 - Sample framework diameter with 960 mm, maximum of 108 (150×70 mm) for the sample installations.

3.3 Compatibilizer Preparation

3.3.1 Preparation and purification of MAH-*g*- HDPE

Modification of the high-density polyethylene with MAH was carried out in a co-rotating intermeshing twin-screw extruder. Lab Tech Engineering twin screw extruder, model LTE26-40, having a screw diameter, D of 26 mm with an L/D ratio = 40, with a rotational speed of 40 rpm. The well pre-mixed materials were then introduced into the hopper of the twin-screw extruder shown in Figure 3.1. The configurations and barrel temperatures were set and controlled for each zone as follows : zone 1 = 378K, zone 2 = 398K, zone 3 = 408K, zone 4 = 418K, zone 5,6 = 423K, zone 7,8 = 433K, zone 9 = 443K and die zone = 443K.

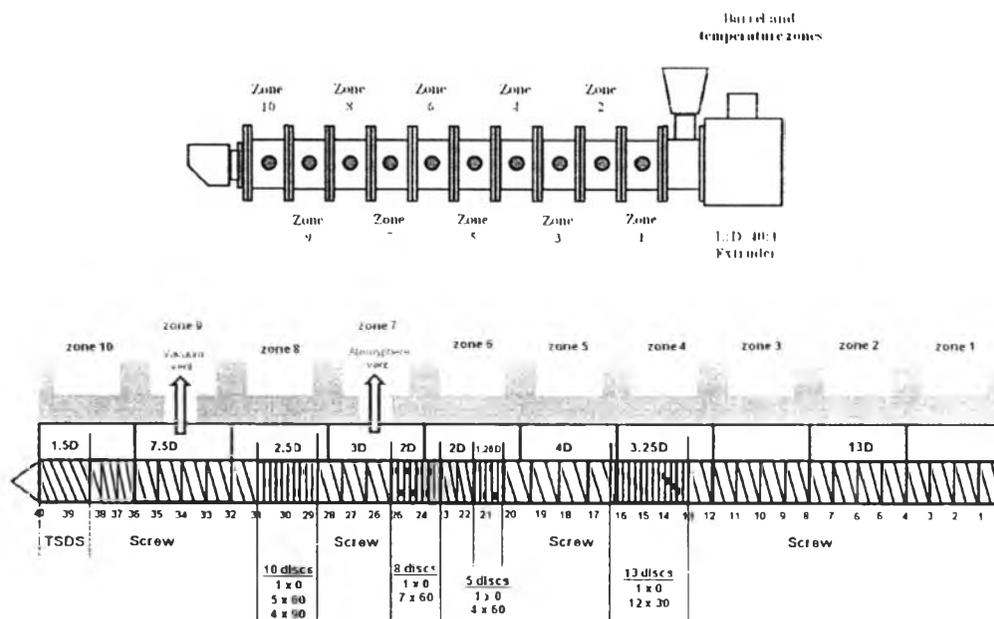


Figure 3.1 Configurations, barrel and temperature zones of the twin-screw extruder

Long-strand extrudates were chopped into granules using the Lab Tech Engineering pelletizer (model LZ-120). MAH was added in the range of 1 to 5 phr based on the polymer, while DCP initiator used was kept constant at 0.5 phr.

Purification was carried out as follows: MAH grafted HDPE (2 g) was dissolved in 100 mL toluene at 333 K for 1 h. After the complete dissolution, the graft copolymer was precipitated by adding acetone at room temperature to remove the unreacted MAH. The precipitated graft copolymer was dried in an oven (Heracus model VTR5022) at 313 K for 24 h to remove the residual solvent.

3.3.2 Determination of the MAH content in the graft copolymer

The quantity of MAH grafted HDPE was determined by titration of the acid groups derived from the hydrolysis of anhydride functional group into carboxylic acid. After the dissolution of 1.0 g of purified MAH grafted HDPE in 100 mL of toluene at the boiling temperature, 0.2 mL of water was added to

hydrolyze the anhydride functionality into the carboxylic acid group. After the solution was refluxed for 2 h to complete the hydrolysis, the carboxylic acid concentration was determined by titration with 0.025 N potassium hydroxide in ethanol in the presence of 1% ethanolic phenolphthalein solution as an acid-base indicator. The carboxylic acid concentration was then converted to the MAH content as follows (Ana, Joao and Figeiro, 2008).

$$\text{MAH (\%wt)} = ((V_0 - V_1) N / 2W) \times 98 \times 100\% \quad (3.1)$$

where N is the concentration (mol/L) of potassium hydroxide dissolved in ethanol. V_0 and V_1 are the volumes of the KOH used in the blank titration and in those titrated with the samples, respectively. W is the weight (g) of the HDPE-g-MAH sample.

3.3.3 Characterization of the compatibilizer system by Fourier Transform IR spectroscopy

The purified MAH grafted HDPE powder was compression-molded into a thin film disc with a thickness of less than 50 μm for Fourier Transform Infrared (FTIR) characterization. Then FTIR spectra of the HDPE-g-MA were recorded using a Fourier Transform Infrared spectrometer (Bruker Tensor 27) with 4 cm^{-1} resolution for 32 scans. For comparison, the pure HDPE, and MAH were also characterized by the IR technique.

เลขที่..... ๒๗. ๒๕๕๓
 เลขทะเบียน..... ๒๐๐๐
 ๑๐ ส.ค. ๒๕๕๓
 หมดอายุ.....

3.4 Blends Preparation

The blends were prepared in the co-rotating intermeshing twin-screw as the one used in section 3.3.1. The weight ratios of ABS and HDPE were 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100. The MAH-*g*-HDPE with the highest grafting degree of MAH onto HDPE chains at a constant content at 2.0 phr was added. Various blend compositions prepared are given in Table 3.1.

Table 3.1 Composition of ABS/MAH-*g*-HDPE/HDPE blends

No.	ABS/MAH- <i>g</i> -HDPE/HDPE (wt%/phr/wt%)	Weight fraction		
		ABS	MAH- <i>g</i> -HDPE	HDPE
1	100/0/0	1.00	0.00	0.00
2	0/0/100	0.00	0.00	1.00
3	80/2/20	0.78	0.02	0.20
4	60/2/40	0.59	0.02	0.39
5	50/2/50	0.49	0.02	0.49
6	40/2/60	0.39	0.02	0.59
7	20/2/80	0.20	0.02	0.78

The well pre-mixed materials were then introduced into the hopper of the twin-screw extruder shown in Figure 3.1. The configurations and barrel temperatures were controlled for each zone as follows : zone 1 = 453 K, zone 2 = 453 K, zones 3,4 = 463 K, zone 5, 6 = 473 K, zone 7, zone 8 = 478 K, zone 9 and die zone = 483 K.

The long-strand extrudates were chopped into granules using the Lab Tech Engineering pelletizer and subsequently dried at 343 K for 6 h.

3.5 Rheological properties

An RH7 Rosand single bore capillary rheometer was used to characterize the flow properties in terms of shear stress and shear viscosity. The tests were carried out at a wide range of shear rates (20 to 9000 s⁻¹) at a test temperature of 473 K. Dimensions of the capillary die used were 1 mm in diameter, 16 mm length and 180° entry angle with an aspect ratio (L/D) of 16:1. The material was first preheated in a barrel for 5 minutes under a pressure of approximately 3-5 MPa to get a compact mass. The excess material was then automatically purged until no bubbles were observed. The test was then carried out at the set shear rate controlled via a microprocessor. During the test, the pressure drop across capillary channel and melt temperature was captured via a data acquisition system. The apparent value of shear stress, shear rate and shear viscosity were calculated using the derivation of the Poiseuille law for capillary flow:

$$\text{Apparent wall shear stress (Pa); } \tau = \frac{R\Delta P}{2L}, \quad (3.2)$$

$$\text{Apparent wall shear rate (s}^{-1}\text{); } \dot{\gamma}_{app} = \frac{4Q}{\pi R^3}, \quad (3.3)$$

$$\text{Apparent shear viscosity (Pa s): } \eta_s = \frac{\tau}{\dot{\gamma}_{app}} \quad (3.4)$$

where ΔP is a pressure drop across the channel (Pa), Q is volumetric flow rate (m^3s^{-1}), R is the capillary radius (m), and L is the length of the capillary (m). The values of R and L used in this work were 1 mm and 16 mm, respectively.

3.6 Thermal analysis

The melting and glass transition temperatures of the blends were studied using DSC200 under a nitrogen atmosphere with a heating and cooling rate of 10 K min^{-1} . The temperature cycle consisted of an initial heating from 303 K to 493 K, followed by cooling to 303 K and a second heating to 493 K. Data were collected during the second heating thermogram.

3.7 Morphological observation

The SEM samples for morphology studies were directly taken from the broken pieces of the blends after the impact test. The sample surfaces were etched with toluene to better reveal the microstructure. Etching was performed at room temperature for 2 h, after which the surfaces were rinsed, dried at 343 K for 6 h. The sample was immersed in 2% OsO_4 aqueous solution for staining the unsaturated components at room temperature for 12 h. After removal from the staining solution, the samples were carefully washed to remove the unreacted

OsO₄. Then the samples were coated with gold to prevent charging before they were examined under SEM observation.

3.8 Mechanical properties

3.8.1 Tensile property measurement

The dumbbell specimens for the tensile property measurement were prepared according to ASTM D4101. They were tested in accordance with ASTM D638. The sample was pulled, by the tensile testing machine, from both ends. The force required to pull the specimen apart, and the extents that the sample was stretched before its breakage were measured.

3.8.2 Flexural strength testing

The flexural test measures the force required to bend a beam under a 3-point loading condition. Test specimens of 3.2 mm x 12.7 mm x 128 mm for the measurement of flexural strength were prepared following ASTM D4101. They were tested according to the standard test method of ASTM D790. The specimen was placed on the two supports and a load was applied at the center. The load at yield measured at a 5% deformation/strain of the outer surface is the flexural strength. The test beam is under compressive stress at the concave surface and tensile stress at the convex surface.

3.8.3 Izod impact strength testing

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. They were

tested according to ASTM D256. A pendulum swing 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 follow through.

3.9 Weathering test

The weathering effect of the blends on the physical and mechanical properties were carried out in a xenon weather meter (Suga Xenon Weather meter). They were tested according to ASTM G155 for 100, 200, and 300 h. At the terminal of weathering time interval, the specimens in the shape for each physical properties testing were removed from the oven and cooled down to room temperature on a flat surface for 24 h before property test. Transparent property was reported in terms of opacity of specimens by using color measurement (GretagMacbeth Instrument Color-Eye 7000A). The weathering resistance was reported in terms yellowness difference (ΔE) of the blends before and after the test using the CIE color difference equation (Larrain, Schaefer and Reed, 2008).

$$\Delta E = (\Delta L^*^2 + \Delta a^*^2 + \Delta b^*^2)^{1/2} \quad (3.5)$$

where ΔL^* is the color difference of light and dark, Δa^* is the color difference of red and green and Δb^* is the color difference of yellow and blue.