

CHAPTER III

EXPERIMENTAL

3.1 Materials

High Density Polyethylene (HDPE) was supplied by Thai Polyethylene Co., Ltd (H6240B); $M_w = 154,870$ (g/mol); $M_n = 12,750$ (g/mol); melting point = 120-130°C.

Methyl Methacrylate (MMA) was supplied by Thai MMA Co., Ltd (stabilized with 4.7 ppm inhibitor); density = 0.944; % Purity = 99.98%.

Dicumyl Peroxide (DCP); a commercial grade from Fluka; %Purity = 97%; half-life time is approximately 1 hr at 135°C and 0.2 hr at 150°C.

All chemicals were used as received.

Silk was supplied from The “SUPPORT” Foundation of Her Majesty Queen Sirikit of Thailand. It was first separated from undesirable matter and degummed then chopped into 6 mm length. Density of silk fiber = 1.16 g/cc (by pycnometer using water as solvent media at 25°C).

3.2 Equipment

3.2.1 Instron Universal Testing Machine

Tensile and flexural properties of the blends were carried out by Instron Universal Testing Machine model 4206.

3.2.2 Zwick Pendulum Impact Tester

Impact properties of the blends were performed by Zwick Pendulum Impact Tester model 5113.

3.2.3 Fourier Transform Infrared Spectrometer (FT-IR)

FT-IR spectra were carried out on Bruker FRA 106/S spectrometer using deuterated triglycinesulfate detector (DTGS) at the resolution of 2 cm^{-1} (16 scans per sample).

3.2.4 Differential Scanning Calorimeter (DSC)

Glass transition temperature (T_g), Crystallization temperature (T_c) and melting temperature (T_m) were determined by Netzch DSC 2000 differential scanning calorimeter.

3.2.5 Thermogravimetric Analyzer (TGA)

Thermal degradation temperature (T_d) of the blends was examined by Du Pont thermogravimetric analyzer TGA2950 under N_2 .

3.2.6 Scanning Electron Microscope (SEM)

A JEOL JSM 5200 scanning electron microscope (SEM) at 5 kV was used to investigate the morphology and the phase structure of the blends.

3.3 Methodology

3.3.1 Silk Degumming and Preparation

Silk was boiled in 1% aqueous solution of C_{14} - C_{16} olefin sulfonate/sodium larylsulfate surfactant solution for 30 min. Then it was rinsed by deionized water for 10 min and allowed to dry in air for 2-3 days. Degummed silk fiber was chopped into 6 mm length approximately. Then it was shredded into single filament in order to increase surface area by an internal mixer.

3.3.2 Preparation of MMA-g-HDPE

MMA-g-HDPE which was used as the compatibilizer was prepared in Brabender Plasti-Corder PL-2000. Firstly, the heating chamber was heated up at 100°C and HDPE was added then mixed for 5 min. Next, 10 % wt of MMA was added in the chamber. According to high temperature of the chamber, MMA monomer can be adsorbed on the surface of HDPE. Then, DCP was added, and the temperature was increased to 160°C leading that the adsorbed MMA on the surface of HDPE can penetrate to the molten HDPE and be grafted on HDPE backbone. The sample was mixed further until the torque was stable. Then the final product was dissolved and refluxed in 50 ml of o-dichlorobenzene at 100°C for 2 hr. The large amount of acetone was added to the solution at room temperature to precipitate the purified MMA-g-HDPE. Therefore, the excess monomer and homopolymer of MMA were washed out.

3.3.3 Preparation of the Blends

The experimental was done comparing between 2 techniques, one-step reactive blending by batch type mixer (Brabender Plasti-Corder PL-2000) and two-step blending by two-roll mill and conventional continuous type mixer (twin screw extruder). The optimum physical and chemical conditions of each technique were given in Table 3.1.

$$\% \text{ volume fraction of silk} = \frac{(g/d)_{\text{silk}}}{(g/d)_{\text{silk}} + (g/d)_{\text{HDPE}}}$$

Table 3.1 Processing physical and chemical conditions of (A) reactive blending and (B) conventional or two-step blending.

Technique	Mixing speed (rpm)	Processing temperature (°C)	%MMA in HDPE	DCP:MMA
A	30	160	10	1:40
B	80	130,150,160,170,180,190	10	1:40

For two-step blending, different mixing sequences were tried out as shown in Table 3.2, and then the dispersion of fibers was observed in each case to determine the best mixing sequence. % weight of MMA in HDPE is 10 %. Then, 10 g of MMA in 90 g of HDPE = Total weight 100 g.

Table 3.2 The effect of the mixing sequences to the dispersion of fiber.

Mixing sequences	Dispersion of fiber
PE, compatibilizer, and silk was added and extruded at the same time in twin screw extruder.	Very poor, fibers are not cooperated with the matrix.
PE and compatibilizer was blended in two-roll mill. Then this blend was added to the twin screw extruder at the same time with silk and extruded to the final blends.	Very poor, fibers are not cooperated with the matrix.
Silk was added to the molten PE in two- roll mill. This blend was added in the twin screw extruder at the same time with compatibilizer and extruded to the final blends.	Intermediate, but fibers still aggregate together, non uniform dispersion.
Silk was added to the blends of PE and compatibilizer on two-roll mill. This blend was extruded by twin screw extruder.	Good, uniform dispersion of fibers.

Thus, the best mixing was obtained in which HDPE was melted on two-roll mill at 160°C for 2 min followed by adding the compatibilizer, purified (MMA-g-HDPE) from 3.3.2, and mixed for another 3 min. Then chopped silk fiber was added, and it was mixed to give a uniform dispersion for 15 min. The blends were shredded and extruded by twin screw extruder with the rotor speed of 80 rpm, and the processing temperature were 130, 150, 160, 170, 180, 190°C according to 6 zones of the extruder. It took 10 min for extruding the final blends. Thus the overall mixing time; the time that silk was subjected to the heat (for both two-roll mill and twin screw extruder); was 25 min.

For reactive blending, the experimental was carried out by Brabender Plasti-Corder PL-2000; batch type mixer. First, the heating chamber was heated up to 100°C, and HDPE was added then mixed for 5 min. The desired amount of MMA was added followed by DCP. The temperature was increased to 160°C leading that the adsorbed MMA on the surface of HDPE could penetrate into molten HDPE and was grafted on HDPE backbone. This step took about 10 min. Silk was added and mixed until the torque was stable (10 min) and uniform dispersion of fiber was obtained. Thus, the time that silk subjected to the heat was 10 min. In addition, the sample was taken from the step just before feeding silk to measure MMA grafting yield and % gel.

3.3.4 MMA-g-HDPE Characterization

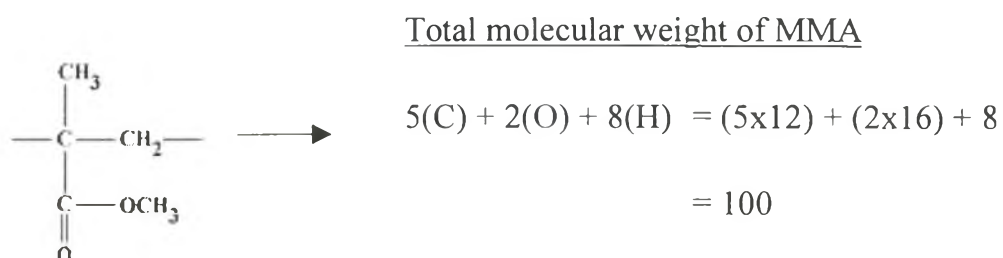
3.3.4.1 MMA Grafting Yield Measurement

After polymerization, the sample of was taken from the step just before feeding silk to measure MMA grafting yield and % gel. Sample (0.5g) was dissolved and refluxed in 50 ml of o-dichlorobenzene at 100°C for 2 hr. Then a large amount of acetone was added to the solution at room temperature to precipitate MMA-g-HDPE part, and the excess monomer and

homopolymer of MMA were washed out. After that purified MMA-g-HDPE samples were dried in vacuum drier for 2 hr to exclude the residual solvent and were pressed into thin films. The percent grafting of MMA onto HDPE was investigated by FTIR spectra of these films by Bruker FRA 106/S spectrometer using deuterated triglycinesulfate detector (DTGS) at the resolution of 2 cm^{-1} (16 scans per sample).

The percent grafting was investigated by comparing the integral ratio between carbonyl stretch in MMA-g-HDPE to the internal reference band which is C-H bending in methyl group of HDPE ($\nu\text{ C=O}$, $1730\text{-}1740\text{ cm}^{-1}$ and $\delta\text{ CH}_3$, 1380 cm^{-1}) in IR spectra. The calibration curve was prepared by melt blending HDPE with polymethyl methacrylate (PMMA). The calibration curve was the plot of integral ratio of carbonyl stretch band ($\nu\text{ C=O}$, $1730\text{-}1740\text{ cm}^{-1}$) to the C-H bending band ($\delta\text{ CH}_3$, 1380 cm^{-1}) as a function of percent weight of MMA in standard samples. The elemental analysis of oxygen; PE 2400 CHNS/O analyzer, was used to calculate the percent of MMA in standard sample as the function of oxygen content. Percentage of MMA in sample was calculated from equation below (Boutevin *et al.*, 1996)

$$\% \text{ weight MMA in sample} = [\text{Experimental oxygen content}^*] \times 100/32$$



Thus:

32 g weight of O ₂	in MMA 100 g
experimental O ₂ content (exp.)	in MMA $\frac{100 \times \text{exp. g}}{32}$

32

* Per unit weight of sample

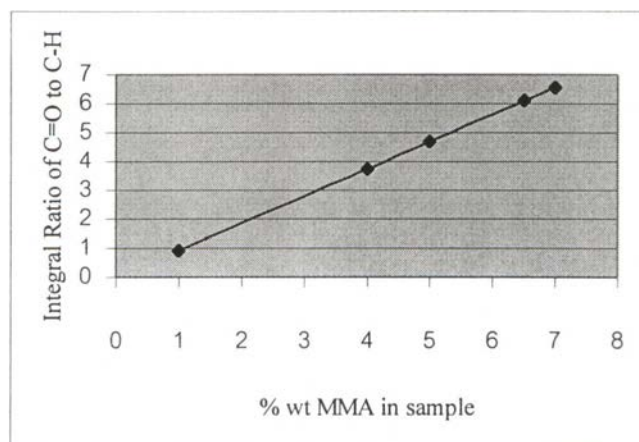


Figure 3.1 The calibration curve of MMA grafting yield measurement.

3.3.4.2 Gel Content Analysis

The crude samples of MMA-grafted HDPE (1g) were refluxed in 100 ml of o-dichlorobezene for 24 hr. After 24 hr the residual portion which was not dissolve will be determined as the insoluble portion (gel) in the sample.

3.3.5 MMA-g- HDPE/ Silk Blends Characterization

3.3.5.1 Mechanical Characterization

To investigate mechanical properties of the blends, the final blends from both techniques were compressed by compression molding at 160°C with preheating time 3 min and applying force 10 ton for 2 min. Tensile testing was done by Instron 4206 testing machine using ASTM D638 test method using dumbell shaped test pieces, at crosshead speed of 50 mm/min. Flexural testing was done by Instron 4206 testing machine using ASTM D790-96a test method at crosshead speed of 1.28 mm/min in a three point loading fitted to 5 KN load cell. Impact resistance was measured using ASTM D256 test method by Zwick impact tester using 2.7 kg striker.

3.3.5.2 Thermal Characterization

Glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were determined by Netzch DSC 2000 differential scanning calorimeter scanning from (-150-150°C) under nitrogen flow at the heating rate of 10°C per min. The midpoint of the slope change of the heating capacity plot in the second scan was determined as the glass transition temperature (T_g), and the maximum of the melting endotherm was considered as melting temperature (T_m). Thermal degradation temperature (T_d) of the blends was examined by Du Pont Thermogravimetric Analyzer under N_2 flow rate of 20 ml/min. The heating rate was 10°C/min from 50°C to 500°C.

3.3.5.3 Morphological Characterization

A JEOL JSM 5200 scanning electron microscope (SEM) at 5 kV was used to study of impact failure specimen surfaces of the blends in order to understand the failure mechanism of the blends in the presence of short fibers. The surfaces of the sample were coated with thin layer of gold before scanned. The morphology, phase structure, fiber dispersion, and fiber matrix adhesion were investigated.