CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1. Polylactide (PLA)

Polylactide resin used is PLA 4042D, a product of Nature Works LLC Co., Ltd, and consists of 92% L-lactide and 8% D-lactide units. The molecular weight is 74,000 g mol^{-1} with a polydispersity index of 2 and a density of 1.25 g cm^{-3} [28]. Its glass transition temperature is about 54-65 °C and melting temperature, T_m is 150 °C. Tensile strength in MD is 16 kpsi, whereas TD is 21 kpsi, Tensile modulus in MD is 480 kpsi, TD is 560 kpsi. The elongation at break in MD is 160%, and TD is 100%. Haze is 2.1% and gloss at 20° is 90%.

3.1.2. Polypropylene (PP)

Polypropylene is a product of TPC (Singapore) Co., Ltd an MFI is at 2.8-3.0 g/10 min, density of 0.9 g cm^{-3}, tensile strength at break of 480 Kg cm^{-2}, elongation of 630%, and melting temperature; T_m is 165 °C. The molecular weight is about 3.2 x 10^5 g mol^{-1}.

3.1.3. Poly[propylene-*graft*-(maleic anhydride)] (PP-*g*-MA)

Poly[propylene-*graft*-(maleic anhydride)] is a product of Sigma Aldrich Co., Ltd. (U.S.A.) consisting of 8-10 wt% of maleic anhydride, average $\overline{M}_n$ is about 3,900 g mol^{-1} determined by GPC, average $\overline{M}_w$ is about 9,100 g mol^{-1} by GPC, melting point is 156 °C, and density of 0.934 g cm^{-1}.

3.1.4. 1,2,3,4-bis(3,4-dimethyl-benzylidene sorbitol); DMDBS

1,2,3,4-bis(3,4-dimethyl-benzylidene sorbitol) is a product of Milliken Chemical Division of Milliken & Co. U.S.A.

3.1.5. Quinacridone red (PR122)

Quinacridone red (beta-form) pigment, (C.I. Pigment Red 122) is a product of Modern Dye Stuff Co., Ltd. Thailand.

3.1.6. Phthalocyanine blue (PB15:3)

Phthalocyanine blue (beta-modification) pigment, (C.I. Pigment Blue 15:3) is a product of Modern Dye Stuff Co., Ltd. Thailand.

3.2 Instrument and Apparatus

Instruments and apparatus for the research are as follows:

1. Twin screw extruder (Lab Tech Engineering, LTE26, Thailand)
2. Cast film extruder (Lab Tech Engineering, Thailand)
3. Differential scanning calorimetry (Mettler Toledo, DSC-822, U.S.A.)
4. Thermogravimetric analyzer (Perkins Elmer, TGA 7, U.S.A)
5. Dynamic mechanical analysis (NETZSCH DMA 242, Germany)
6. Universal testing machine (LLOYD model LRX PLUS, UK)
7. Haze meter (BYK-Gardner model Haze-gard dual, Germany)
8. Densitometer (Macbetch model TD931, U.S.A.)
9. Polarized optical microscope (Leica DM LB, Germany)

10. Fourier-Transform Infrared spectrometer (Perkins Elmer Spectrum I, U.S.A.)

11. Scanning electron microscope (JEOL JSM-5410LV, Japan)

12. X-Ray diffractrometer (JEOL model JDX-8030, Japan)

3.3 Procedure

3.3.1 Compounding

Polypropylene/polylactide blends were prepared with the following compounds using a twin screw extruder from Labtech Engineering model LTE 26 (L=40D, D=26 mm). The twin screw extruder is a co-rotating screw type (Figure 3.1) and processing temperature profile is shown in Table 3.1. To ensure the moisture content below 250 ppm, Karl Fisher titration method was applied to the polylactide after it had been dried in an oven at 90 °C overnight. The compound formulations without and with nucleating agents are summarized in Table 3.2 and Figure 3.2.

Figure 3.1 : Twin screw extruder.

Table 3.1 Temperature profile of the twin screw extruder

Zone	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	90	150	210	220	220	220	220	220	220	220

Table 3.2 Compound formulations without nucleating agents

Blends Ratio	Polypropylene(%)/Polylactide(%)/PP-*g*-MA(%)		
	90/10/0	80/20/0	70/30/0
	90/10/5	80/20/5	70/30/5

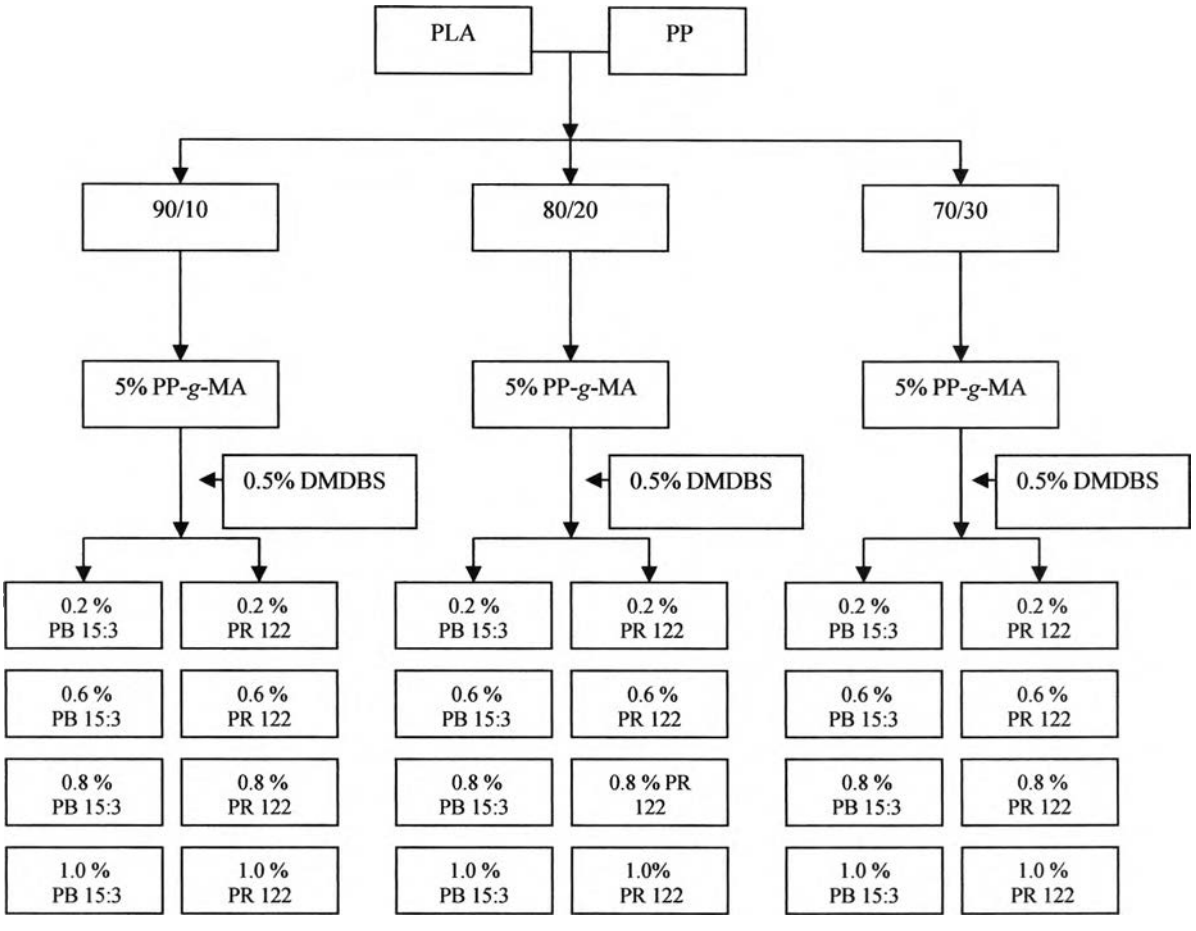


Figure 3.2 : Compound formulations with the pigmented nucleation.

The temperature was controlled at all zones and die zone by following the temperature profile as illustrated in Table 3.1. The speed was fixed at 80 rpm. The long strand extrudates were cooled in a water bath and chopped into pellets using a pelletizer and subsequently they were dried at 90 °C overnight before testing.

3.3.2 Characterization of thermal properties by differential scanning calorimetry (DSC)

Thermograms were obtained from a Mettler Teledo model DSC 822 differential scanning calorimeter (DSC). The calibration was done with indium tin oxide in the temperature range from 25 °C to 200 °C. Stainless pans were used and the sample mass was weighed approximately 10 mg. All pelletized samples were first cycle heated from 25 °C to 200 °C with a scan rate of 20 °C min^{-1} to get rid of any previous thermal history, held at 200 °C for 5 min, cooled down to 25 °C with a scan rate of 5 °C min^{-1}, then heated from 25 °C to 200 °C again with a scan rate of 10 °C min^{-1}. The percentages of crystallinity and enthalpy were determined using a constant integration of peak area. The DSC feature is shown in Figure 3.3.

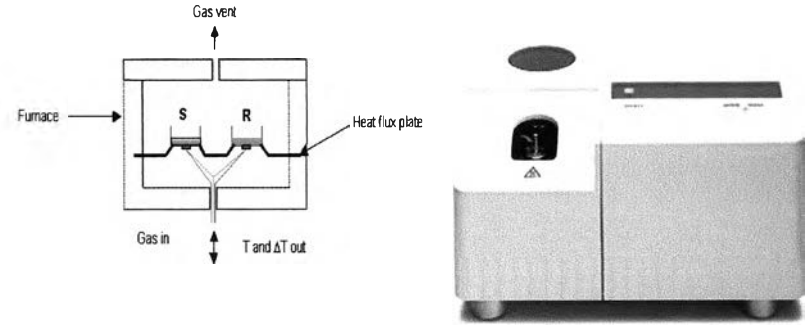


Figure 3.3 : Typical DSC cells including the sample and reference.

3.3.3. Characterization of thermal degradation by thermal gravimetric analyzer (TGA)

Thermal analysis of the samples was determined using Perkins Elmer model SDT 2960, U.S.A. It measured the changes in weight loss of the materials with increasing temperatures. The TGA data of the polymer blends were obtained by heating the samples under a nitrogen atmosphere at a heating rate of 20 °C min^{-1} to the final temperature of 700 °C.

3.3.4 Determination of dynamic mechanical properties by dynamic mechanical analysis (DMA)

DMA data, storage modulus (E′), loss modulus (E″), and loss tangent (tanδ), were obtained at 1 Hz with NETZSCH model DMA 242, Germany. The measurement was performed by a dual cantilever bending mode with a sample specimen dimension of 32.00 mm x 9.87 mm x 2.20 mm under a nitrogen atmosphere at a heating rate of 3 °C min^{-1} from -50 °C to the final temperature of 120 °C. The ends of the sample were tightly clamped before testing. This arrangement is especially suitable for the samples having a mixed modulus range (rubber and thermoplastics). The DMA feature is shown in Figure 3.4.

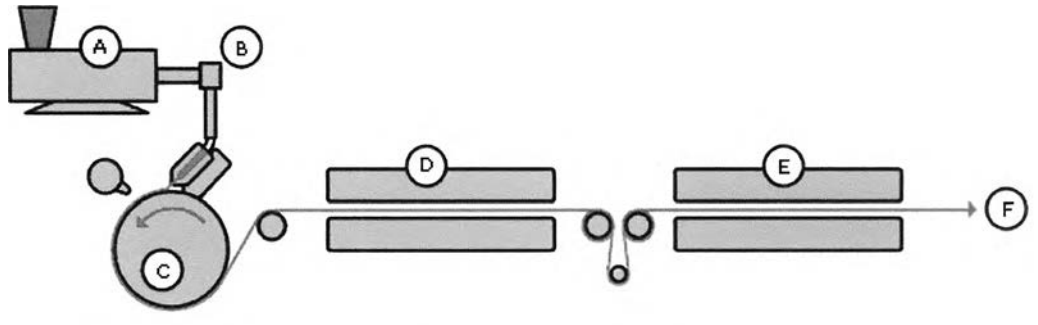
Figure 3.4 : A DMA schematic of dual cantilever.

3.3.5 Cast film extrusion process

Single screw extrusion is a continuous process in which the polymer is melted, the molten polymer is then forced through a flat die. The obtained extrudate is a flat sheet film and passed through a chilled roll to cool the film. The temperature profile of cast film extrusion is shown in Table 3.3 and the cast film line scheme is shown in Figure 3.5.

Table 3.3 Temperature profile of a cast film extrusion

Zone	1	2	3	4	5	6	7	8	9	10	11
Temperature (°C)	160	180	220	220	240	240	240	240	245	245	245



(A) Extruder (B) Melt pump (C) Chill roll (D-E) Stretching MD (F) Winding film.

Figure 3.5 : Cast film line scheme.

3.3.6 Characterization of mechanical properties by universal tensile testing machine

The experimental method followed ASTM D 882-97 in which tensile strength, modulus, and elongation at break were measured by using Universal Tensile Testing Machine; LLOYD model LRX plus, U.K. with a grip head speed at 200 mm min^{-1} with 500 N loading. All film samples were cut from each component of the cast film extrusion with a film thickness of 50 micrometers, then died cut with CEAST apparatus with a dimension of 2.5 cm x 12 cm. For each formulation, 10 specimens were tested in the machine direction (MD) and 5 data were chosen to report the tensile strength (MPa), elongation (%), and modulus (MPa) for accurate data.

3.3.7 Characterization of crystalline morphology by polarized optical microscopy (POM)

The PP and PP/PLA/PP-*g*-MA blend film samples were pressed between the micro-glass at 200 °C for 1 min and were air cooled to room temperature. The samples were observed with a 40 x optical zoom objective lenses in a Leica DM LB polarized optical microscope (POM). The crystalline morphology of the sample was obtained.

3.3.8 Characterization of blend morphology by scanning electron microscopy (SEM)

The cryofractured surfaces of the PP/PLA blends were investigated using a scanning electron microscopy (SEM, model JDX-8030, JEOL, Japan). The thickness of gold coating on the samples was 25 nm, and SEM was operated with an accelerating voltage of 15 KV to give a good image contrast.

3.3.9 X-ray diffraction analysis (XRD)

X-ray diffraction measurements were performed using an X-ray diffractometer, JEOL model JDX-8030 (CuKα radiation, 20 KV, 40 mA, with λ = 0.15406 nm and n = 1) at a scanning range from 5-30° and a scanning rate of 0.025 ° min^{-1}. The interlayer of crystal was calculated using Bragg's equation (Equation 1) :

$$n\lambda = 2d\sin\theta \qquad \text{(Eq.1)}$$

where d is the interplanar distance of reflection plane, θ is the diffraction angle, λ is the wavelength.

3.3.10 Identification of functional groups by Fourier-Transform infrared spectrometry (FT-IR)

The function groups of the PP/PLA/PP-*g*-MA blends and pigments were identified using Fourier-Transform Infrared Spectrometry (FT-IR) (Perkins Elmer, model Spectrum I). The sample was prepared as a hot pressed film and subjected to FT-IR spectrometric technique.

3.3.11 Haze measurement

The test was carried out by measuring the transmitted light which, in passing into the transparent specimen thickness of 50 micron, the light may deviate and scatter more than 2.5 degree on the average. The specimens were prepared by casting film having a thickness of about 50 micrometer. It was observed by a haze gard dual (BYK-Gardner) (See Figure 3.6) following the procedure described in ASTM 1003. Each sample was repeated five times.

Figure 3.6 : Haze meter.

3.3.12 Opacity measurement

The opacity measurement indicates the distribution capacity of a pigment in film by measuring the intensity of transmitted light. If density of the light required to transmit through the film is thus high, the opacity of film is low. Thus this method of opacity measurement is reported in terms of density of light and %Dot. %Dot value indicates the percentage of light transmission using a densitometer.