

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

PP pellet grade 1100NK (MFI = 10.8 g/10 min, MFI<sub>2.16, 230°C</sub>) and ethyl-vinyl acetate (VA) copolymer (EVA) grade MV1055 containing 28 wt % vinyl acetate (MFI<sub>2.16, 190°C</sub> = 8 g/10min.) cordially supplied by Thai Petrochemical Industry Public Co., Ltd. (TPI) were used as received.

Dicumyl peroxide (DCP, Akzo Chemie), maleic anhydride (MA, Grand Union Chem Co., Ltd.), Irganox1010 (Akzo chemie) were also used as received.

#### 3.2 Instruments

Followings are the list of major instruments used in this study.

1. PL-2000 Brabender Plasti-Corder (BPC) with other compartments such as a DSK 42/7 twin screw extruder and a 881201 Bradender pelletizer. The screw configuration was of intermeshing counter-rotating type with 41.8 mm screw diameter, 7D screw length, 6.45 mm depth of thread and 10 mm pitch.
2. 258D Pendulum impact tester
3. LR10K Lloyd universal testing machine
4. DXT-3 Matsuzawa Hardness Tester (Rockwell)
5. IS100G 100MT Toshiba injection molding machine
6. MPX 62.92 Gottfert Melt Flow Indexer
7. DSC7 Perkin-Elmer Differential scanning calorimeter (DSC)
8. S-25000 Hitachi Scanning Electron Microscope (SEM)

### 3.3 Experimental

#### 3.3.1 Preparation of PP Powder

Polypropylene (PP) powder employed in this study was produced by TPI using a laboratory scale 20 L stainless steel autoclave. The gas phase polymerization was controlled at  $70 \pm 2^\circ\text{C}$  for 1.5 h with the propylene and hydrogen gas pressure constantly during the experiments at 28 bar and 10 bar (measured from metering pot), respectively. The Ziegler-Natta catalyst used was  $\text{TiCl}_4/\text{Al}(\text{Et})_3$  supported on  $\text{MgCl}_2$ . The PP powder produced had the melt flow index (MFI) at  $2.16 \text{ kg}/230^\circ\text{C}$  ( $\text{MFI}_{2.16, 230^\circ\text{C}}$ ) of  $3.17 \text{ g}/10 \text{ min}$ .

#### 3.3.2 Grafting Maleic Anhydride onto Polypropylene

Weigh 500 g PP powder ( $\text{MFI}_{2.16, 230^\circ\text{C}} = 3.17 \text{ g} / 10 \text{ min}$ ), fixed amount in phr of DCP and MA and introduce into a plastic bag. Table 3.1 shows the amount of DCP and MA, and the screw speed of twin screw extruder employed in the experiments at various screw speeds. Then hand-mixing the materials for 15 minutes. The mixed materials were subsequently fed into a hopper of the twin screw extruder which the temperature of three heating zones was controlled at  $190^\circ\text{C}$  and of die zone was at  $157^\circ\text{C}$ . The long strand extrudates were chopped into granules using the pelletizer.

PP-g-MA Granules of each experiment were mixed with 2 phr Irganox 1010 in a plastic bag for 15 minutes. Then the mixed materials was reextruded using the twin screw extruder with the controlled heating zones at  $200^\circ\text{C}$  (1st),  $210^\circ\text{C}$  (2nd),  $210^\circ\text{C}$  (3rd) and the die zone at  $210^\circ\text{C}$ ; the screw speed was fixed at 40 rpm. The extrudates were also chopped in the form of granules using the pelletizer, and subsequently dried at  $70^\circ\text{C}$  for 12 h and kept in a plastic bag under nitrogen atmosphere.

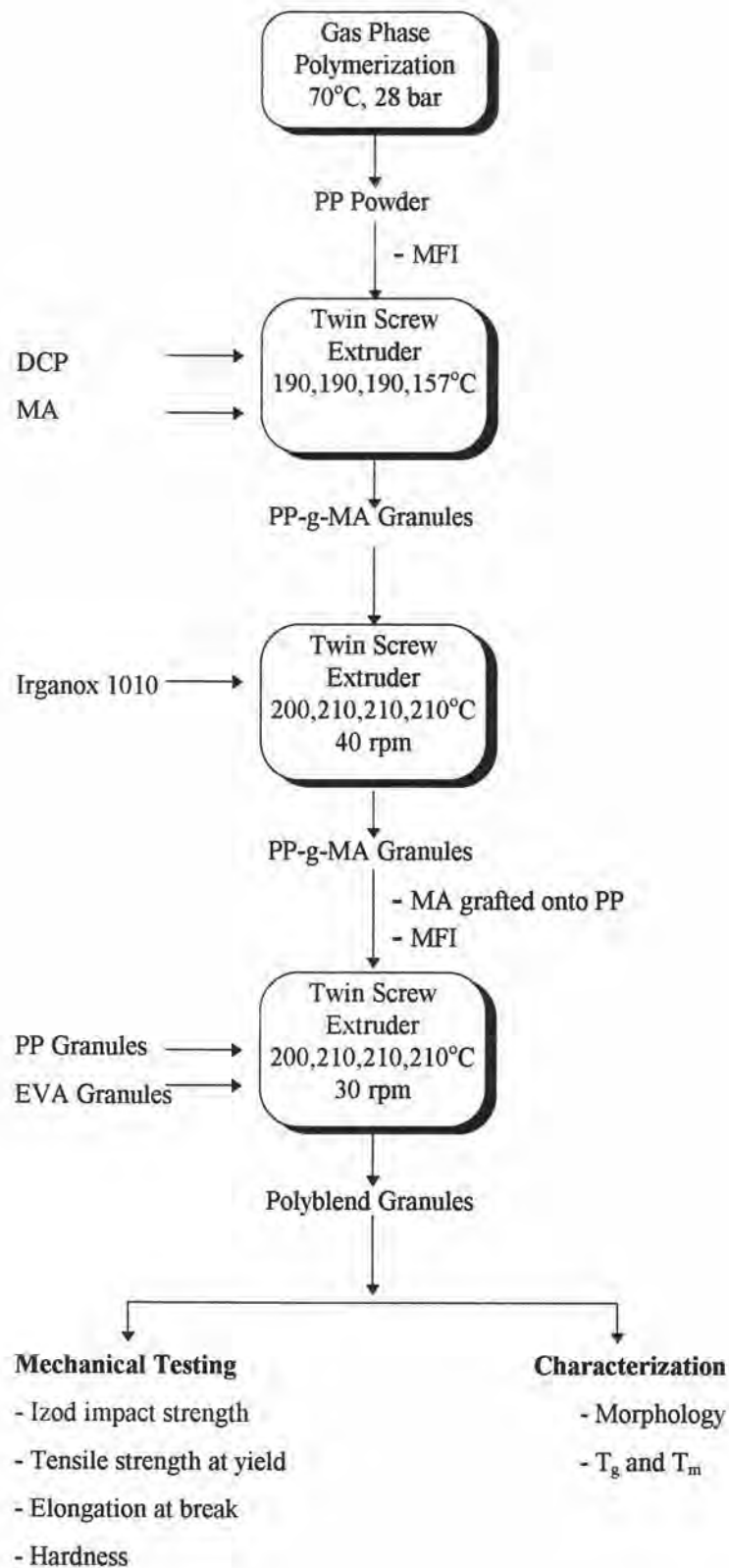
**Table 3.1** Quantities of DCP and MA, and the screw speeds of twin screw extruder employed for the preparation of maleic anhydride grafted PP (PP-g-MA).

Screw Speed (rpm)	DCP (phr)	MA (phr)
100	1.0	5.0
90	1.0	5.0
80	1.0	5.0
60	1.0	5.0
90	1.0	5.0
90	2.0	5.0
90	3.0	5.0
90	4.0	5.0
90	4.0	5.0
90	4.0	5.5
90	4.0	6.0
90	4.0	6.5
90	4.0	7.0
90	4.0	8.0

### 3.3.2. Preparation of PP and EVA (PP/EVA) Blend

The total amount of 1700 g PP and EVA pellets were used for the preparation of PP/EVA blend. The amount of EVA in the polyblends varied from 0, 5, 10, 20, 30, 40 to 50% by weight. Each of the blend composition, PP-g-MA (0.7% MA grafting onto PP) was used as a compatibilizer ranging from 0, 2, 4, 6 to 10 phr.

Typically all of the materials mentioned above were dried mixing in a LMX 5W Lab Tech mechanical mixer for 10 minutes. Except when the EVA amount was greater than 30% by weight, hand-mixing was carried out in a plastic bag by tumbling up and down for 30 minutes. The mixed materials were then introduced into a hopper of the twin screw extruder, with the controlled temperature of three heating zones at 200°C (1st), 210°C (2nd) and 210°C (3rd), and of the die zone at 210°C; the screw speed was fixed at 30 rpm. The long strand extrudates were chopped into granules using the pelletizer and subsequently dried at 70°C for 12 h. They were kept in a plastic bag sealed with nitrogen gas prior to use.



**Figure 3.1** Diagram of experimental procedure to prepare PP-g-MA and PP/EVA blend.

### 3.4 Characterization of PP-g-MA

#### 3.4.1 Determination of Maleic Anhydride Content [14]

Unreacted MA presented in the PP-g-MA granules was eliminated using reflux technique. 2 g PP-g-MA and 250 ml xylene were introduced into a 500 mL conical flask containing a magnetic bar and fitted with a condenser. A magnetic hot plate was used to provide heat to the system until xylene boiled; it remained for about 45 minutes. Then the hot solution was slowly and carefully added into 200 ml acetone to obtain PP-g-MA precipitate. Recovered PP-g-MA was achieved by vacuum filtration technique and finally rinsing by acetone; the unreacted MA remained in the filtrate. The purified PP-g-MA was dried in an oven at 70°C for 12 h.

0.5 g purified PP-g-MA was dissolved in 75 mL boiling xylene for 60 min in a 250 mL conical flask. The hot solution was then titrated with 0.005 N ethanolic KOH using phenolphthalein as an indicator. The end point could be observed by the change from the colorless to pink solution. Then a 1-mL excess KOH solution was added, and a deep pink color was back titrated to a colorless end point using 0.005 N isopropanolic HCl. The experiments were repeated at least three times. The weight percentage of MA grafting on PP was calculated by Equation (3.1). PP powder that used as the starting materials for preparation of PP-g-MA was used as a blank followed the method described above. Therefore, the average values of MA content in the grafted polymer reported subsequently are those already subtracted by the blank values.

$$\%MA \text{ onto PP} = \frac{(\text{mole of KOH} - \text{mole of HCl}) \times 98 \text{ g.mole}^{-1} \times 100}{\text{weight of sample (g)}} \quad (3.1)$$

#### 3.4.2 Measurement of MFI

MFI measurements were carried out on a MPX 62.92 Gottfert at 230°C with the hammer load of 2.16 kg in accordance with ASTM 1238.

### **3.5 Mechanical Properties**

#### **3.5.1 Izod Impact Strength Testing**

Test specimens for the measurement of Izod impact strength were prepared following ASTM D4101. They were tested according to the standard method of ASTM D256.

#### **3.5.2 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.

#### **3.5.3 Measurement of Hardness**

The rockwell hardness specimens were prepared following ASTM D4101 They were tested in accordance with ASTM D785.

### **3.6 Differential Scanning Calorimetric Technique**

#### **3.6.1 Determination of Melting Temperature ( $T_m$ )**

25 mg sample was heated from 50 to 200°C under nitrogen atmosphere using a heating rate of 200°C/min, and held for 10 min. The sample was then cooled from 200 to 30°C at 10°C/min and hold for 5 min. After that, the sample was heated from 30 to 190°C at 10°C/min. Data were collected during the second heating cycle.

### **3.6.2 Determination Glass Transition Temperature ( $T_g$ )**

Samples were melted at 180°C for 15 min in order to destroy processing and thermal memory, and subsequently annealed in an oven at 80°C for 8 h. Then 25 mg of that sample was heated from -60 to 60°C using a heating/cooling rate of 5°C/min. Data were collected from the first scan.

### **3.7 Morphology of Polymer Blends**

Scanning electron microscopy (SEM) was used to observe the morphology of polymer blends. The specimens were immersed in liquid nitrogen for 30 min, then were broken rapidly. The broken surface was coated with platinum-palladium using T-102 Hitachi coating unit.