CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Homopolymer polypropylene resin (Pro-fax 6531) supplied by HMC Polymers Co., Ltd., Rayong, Thailand. MFI loaded by 2.16 kg at 230 °C of 4.0 and density of 0.905 g/cm^3.
2. Heterophasic copolymer or PP/EPR blends (Pro-fax SW7533) supplied by HMC Polymers Co., Ltd., Rayong, Thailand. MFI loaded by 2.16 kg at 230 °C of 5.0 g/10min and density of 0.905 g/cm^3.
3. Pimelic acid (Heptanedioic acid; $C_7H_{12}O_4$) supplied by Fluka Chemie Gmbh, Switzerland. Melting point of 103°C and boiling point of 272°C.
4. Calcium stearate supplied by SUN ACK Kakoh, Korea.
5. Talcum Haichen 37, average particle size 3.5 μm, China.
6. Concentrated sulfuric acid suppied by MERCK KcaA., Germany.
7. 90% Phosphoric acid from BDH Laboratory Suppliers, Poole, England.
8. Potassium permanganate ($KMnO_4$) from Carlo Erba, Milano, Italy.

3.2 Instruments

Major instruments used are listed below:

1. HAAKE Polylab® system twin screw extruder (Germany).
2. RP 25C1 Pelletizing unit (Thai Hydraulic Machinery Co., Ltd., Thailand).
3. 50L high speed mixer (Cheng Ta Iron Work Co., Ltd., Feng Shang, Kaohsiung, Taiwan)
4. SUMITOMO Injection molding machine (Japan).
5. CEAST melt flow indexer (Italy)
6. INSTRON model 4466 and 4302 universal testing machine (England)

7. Perkin-Elmer thermal analysis system model DSC-7 Differential scanning calorimeter (Connecticut, USA.)
8. Standard weight class E2 size 1 – 500 g (Switzerland)
9. Standard weight class F1 size 5 kg (Switzerland)
10. Mitutoyo Dial micrometer 0-5 mm. (Japan)
11. JEOL JSM 5410 LV Scanning electron microscope (Japan)
12. PENDULUM 25J Izod impact tester (Italy)
13. CEAST HDT/ Vicat tester (Italy)
14. PRECISION lab. oven model STM135 (USA.)
15. JEOL JDX-8030 x-ray diffractometer (Japan)

3.3 Experimentals

3.3.1 Preliminary study on β-nucleator selection.

In this study, many types of β-nucleator was firstly blended with PP/EPR blends for selection one type which shown highest in mechanical properties one. These blends were prepared as 5 formulas:

1) PP/EPR blended without β-nucleator as control
2) PP/EPR blend filled with 0.1 wt% of DMDBS
3) PP/EPR blend filled with 0.1 wt% of Sodium Benzoate (NaBz)
4) PP/EPR blend filled with 0.1 wt% of Talcum
5) PP/EPR blend filled with 0.1 wt% of Ca-Pim.

Each formulation was first physical blend in 50L high speed mixer throughout melt-mixed in twin screw extruder at 190/200/210/220°C (from hopper to nozzle), 95 rpm and then pelletized with granulator. These pallet samples were molded to form dumbbell shape specimen and impact specimen for mechanical properties testing by injection molding machine at 185/195/200/205/210°C (from hopper to nozzle).

3.3.2 Preparation of talc-filled with and witout β-nucleator to homopolymer PP and/or PP/EPR blend.

The homopolymer polypropylene (HM) and heterophasic copolymer of PP/EPR blends (HC) were thoroughly dry mixing with and witout added three types of nucleator; talcum, pimelic acid and calcium stearate, by using a high speed mixer according to the compositions show in Table 3.1. All these blends were performed on a small scale co-rotating twin screw extruder with a screw diameter of 41.8 mm, length of 7D and output rate ~ 3.0 kg/hr. The temperature profile commenced from hopper zone, three barrel zones till die head, was 190, 200, 205, 215 and 220 °C, respectively. Strand exiting the extrudate was immediately quenched in a water bath and subsequently pelletized to afford pellet samples before molded to form dumbbell shape specimen and impact specimen for mechanical properties testing by injection molding machine at 185/195/200/205/210°C (from hopper to nozzle), mold temperature of 60°C, and packing time 35 sec.

Table 3.1 The formulations of HM or HC blends with and without added nucleators.

Sample code	Nucleator added (% wt)		
	Talc	Pimelic acid	CaSt
HM 0	-	-	-
HM 1	30 %	0.10 %	0.10 %
HM 2	40 %	0.10 %	0.10 %
HC 0	-	-	-
HC 1	30 %	-	-
HC 2	40 %	-	-
HC 3	30 %	0.10 %	0.10 %
HC 4	40 %	0.10 %	0.10 %

3.3.3 Preparation of PP/EPR blends added with various amount of pimelic acid and calcium stearate

The blend of PP/EPR (IC) added with various amount of combination of pimelic acid and calcium stearate (CaSt) which acted as β-nucleator were prepared to form mechanical testing samples the same as section 3.3.2. The formulations of these blends show in Table 3.2.

Table 3.2 The formulations of PP/EPR blends added various amount of pimelic acid and calcium stearate.

Sample code	β-nucleator added (wt%)	
	Pimelic acid	Calcium Stearate
PP/EPR_0 (IC_0)	0.0000	0.0000
PP/EPR_1 (IC_1)	0.0005	0.0005
PP/EPR_2 (IC_2)	0.0050	0.0050
PP/EPR_3 (IC_3)	0.0125	0.0125
PP/EPR_4 (IC_4)	0.0250	0.0250
PP/EPR_5 (IC_5)	0.5000	0.5000

3.4 Characterization and measurements.

3.4.1 Mechanical properties

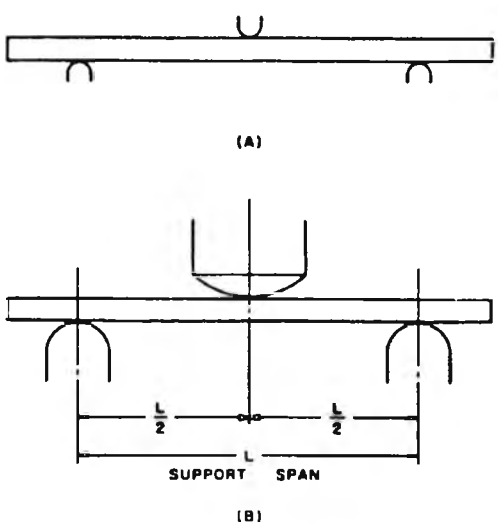
3.4.1.1 Determination of tensile properties.

The dumbbell shaped specimens which molded from injection machine (from sections 3.3.1-3.3.3) were measured following the procedures described in ASTM D638 method A using a universal testing machine, Instron model 4466, with a computer controlled measurement system.

The tensile parameters and testing condition, speeding testing of 500 mm/min, gauge length of 50 mm., load cell of 50.99 Kg_f and temperature at 23 ± 2 °C, were used. The measurement of tensile strength at yield (Kg_f/mm^2) and elongation at yield (%) were made with six specimens in each blend.

3.4.1.2 Determination of flexural modulus

The dumbbell shaped specimens which molded from injection machine (from sections 3.3.1-3.3.3) were performed with ASTM D790 method A using universal testing machine, Instron model 4302, with a computer controlled measurement system, three point loading system (Figure 3.1) with diameter of support rods and loading rod at 4 and 10 mm., respectively. The condition of testing specimen was set at 23±2°C and -50±5% relative humidity for not less than 40 hrs. prior to test accordance with method A. The flexural modulus (MPa) was measured with six specimens in each blend.



Note: (A) Minimum radius = 3 mm. (B) Maximum radius supports = 1.5 times specimen depth, maximum radius loading nose = 4 times specimen depth.

Figure 3.1 Loading nose and support diagram 3-point loading

3.4.1.3 Determination of impact strength

The impact test specimen with dimension of 6.35 by 1.27 by 0.64 cm and 0.0254 cm of notched radius (from injection molded in sections 3.3.1-3.3.3) with six specimens in each blend was accomplished on a PENDULUM 25J Izod impact tester. The test procedure conformed to the ASTM D256 method A. Each specimen was held as a vertical cantilever beam and broken by a single swing of the pendulum with the line of initial contact at a fixed distance from the specimen clamp and from the centerline of the notch and on the same face as the notch. The line of contact of the striking nose is located at the center of percussion of the pendulum within ±2.54 mm. (0.10 in.). Store the test specimens at 23±2°C and 0±5% relative humidity for not less than 40 hrs. after notching and prior to measuring.

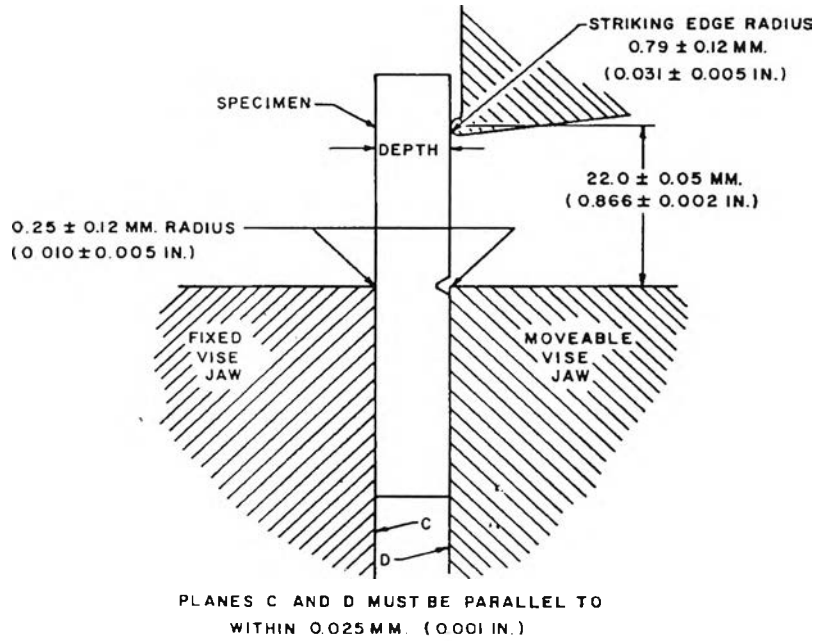


Figure 3.2 Relationship of vise, specimen, and striking edge to each other for Izod test method A and C

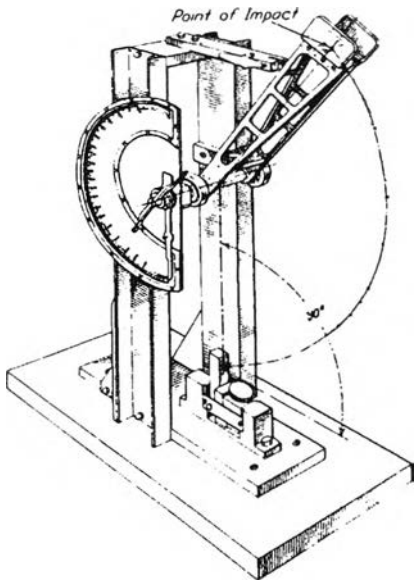
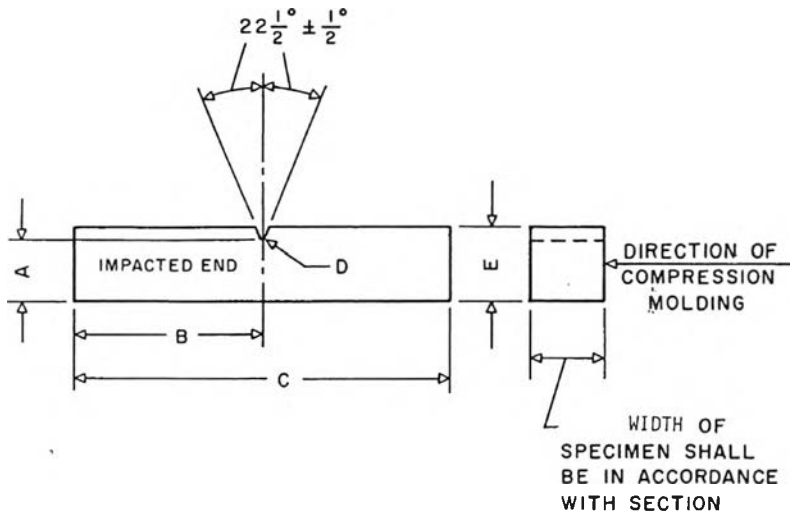


Figure 3.3 Cantilever beam (Izod-type) impact machine



	mm	in.
A	10.16 ± 0.05	0.400 ± 0.002
B	32.00 max	1.260 max
	31.50 min	1.240 min
C	63.50 max	2.500 max
	60.30 min	2.375 min
D	0.25R ± 0.05	0.010R ± 0.002
E	12.70 ± 0.15	0.500 ± 0.006

Figure 3.4 Dimensions of Izod type test specimen

3.4.2 Thermal analysis

The pallets sample from extrusion process were measured the melting temperatures (T_m) and crystallization temperature (T_c) by using a Perkin-Elmer model DSC-7. Indium and zinc standards were used for temperature calibration. This sample weighing about 5 mg. was put into a DSC sample pan and melted in a furnace in nitrogen atmosphere from 40 to 220°C at a heating rate of 20°C/min, following by 20° C/min cooling. T_m and T_c were determined during cooling and second heating. The peak temperature of the exothermic curve was taken as T_c, whereas the endothermic curve was T_m.

3.4.3 Morphology study of β-form PP samples

The pallets sample from extrusion process was compressed to form film samples thick ~ 0.3 mm using compression molding and then etched with a 0.7 wt% solution of $KMnO_4$ in a 2:1 (v/v) mixture of concentrated sulfuric acid and 90% phosphoric acid for 3 hrs. at room temperature. The etched samples were washed with a 2:7 (v/v) mixture of concentrated sulfuric acid and water, the washed with demineral water again, and finally dried in a conditioning room (temperature 23±2 °C, relative humidity 60±5%). After that they were mounted on SEM stubs with a thin layer of gold was evaporated on the samples prior to SEM examinations.

3.4.4. X-ray diffraction measurement

The pallets sample from extrusion process was compressed to form thinning plate by thinning compression mold plate and then measured the X-ray diffraction patterns using the X-ray diffractometer with flat-film geometry. Nickel-filtered CuK_α radiation (λ = 0.154187 nm) operated at 50 kV and 30 mA was employed. The patterns were recorded with the incident X-ray beam positioned at the angle 2θ = 10-80 degrees to the film surface. This technique is generally used to

investigate the crystal structure. The K-value corresponding to the relative amount of the β-form was calculated using following formula

$$K = \frac{H_\beta(300)}{H_\beta(300) + H_\alpha(110) + H_\alpha(040) + H_\alpha(130)}$$

Where $H_\alpha(110)$, $H_\alpha(040)$ and $H_\alpha(130)$ are the intensities of the X-ray diffraction of the α-reflection and $H_\beta(300)$ is the intensity of the reflection measured as the height of the peaks. The K-value tends to zero if no β-form is present and to unity in the case when a lot of β-form is also present, i.e. α-form is almost absent.