



CHAPTER III METHODOLOGY

3.1 Materials and Equipment

3.1.1 Materials

The materials used in this study were ENR with 25 % epoxidation, supplied by Muang Mai Guthrie PCL., NBR (grade KRYNAC 3345F), supplied by PI Industry Ltd., PVDF (grade Z100), supplied by Asambly Chemicals Company, PLA (grade 2002D), supplied by NatureWorks LLC. The selected additives (Fluka reagent grades) were calcium hydroxide ($\text{Ca}(\text{OH})_2$) and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (DBPH). Triacetin was supplied by Sigma-Aldrich Co. LLC. Stearic acid and triallyl isocyanurate (TAIC) were purchased from Neo plastomer Co.,Ltd. Organoclay with surfactant type of DEHYQUART[®] F 75. Gasohol 91, 95, E20 and E85 were supplied by PTT PCL.

3.1.2 Equipments

3.1.2.1 *Internal Mixer*

An internal mixer was a Brabender Plasti-corder 815602 type. It was manufactured by Brabender[®] OHG Duisburg (Germany) and supplied by Melchers Techexport GMBH (Bremen, Germany). The mixer was N50 with a chamber capacity of 80 g. It used 1 kW drive unit.

3.1.2.2 *Two Roll Mill*

The two roll mill was a LRM 110 model with a capacity of 200 g which was manufactured by Labtech Engineering Co., Ltd (Bangkok, Thailand).

3.1.2.3 *Twin-Screw Extruder*

The twin screw extruder was manufactured by Lactech Engineering Co., Ltd (Bangkok, Thailand). It was a LTE20-40 model with a L/D ratio of 40/1. The barrel cavity was 200 g and die pressure capacity was 100 bar.

3.1.2.4 Cooling Bath

The cooling bath was a Labtech LW-100 model. Water was used as a coolant which was pumped into the cooling bath by using Labtech water pump LCW-80 model.

3.1.2.5 Pelletizer

The pelletizer was a Labtech LSC-108 model which used for cut pellets. It was manufactured by Labtech Engineering Co., Ltd (Bangkok, Thailand).

3.1.2.6 Compression Mold

The compression mold was a V50H-18-CX model with a compress capacity of 50 ton which was manufactured by Wabash MPI (Indiana, USA) and supplied by Intro Enterprise Co., Ltd (Bangkok, Thailand).

3.1.2.7 Moving Die Rheometer (MDR)

The MDR was a rheoTECH MD+ model which was supplied by CG Engineering Ltd., Part.

3.1.2.8 Rheometer

The rheometer was a ceast 5000 model, 7037000 type (Pianezza-Torino, Italy) which was supplied by Instron, Ltd (Bangkok, Thailand).

3.1.2.9 Differential Scanning Calorimeter (DSC)

The DSC822E model was supplied by Mettler Toledo, Ltd (Bangkok, Thailand).

3.1.2.10 Universal Testing Machine (UTM)

The UTM was a 4206-006 model which was supplied by Instron, Ltd (Bangkok, Thailand). It was used to measure the tensile strength, percent elongation at break, young's modulus and tear strength.

3.1.2.11 Durometer

The durometer was a Zwick, 7206 type which was used to measure the hardness of samples.

3.1.2.12 Dynamic Mechanical Analyzer (DMA)

The DMA was a GABO-EPLEXOR 100N model which was manufactured by GABO – QUALIMETER Co.,Ltd.

3.1.2.13 Field Emission Scanning Electron Microscope (FE-SEM)

The SEM was a HITACHI S-4800 model which contributed the images in the magnification range of 1,000 to 10,000 times at 10 kV. The samples must be coated with platinum under vacuum condition before observation to make them electrically conductive.

3.1.2.14 Air Oven

An air oven was used for accelerating the age of specimens in case of aging test. The specimens must be tested within 96 h after aging.

3.2 Preparation of The Blends

3.2.1 Preparation of Rubber Parts

The ENR and NBR compound were prepared for curing characterization by using MDR and DSC. They were blended by using an internal mixer at room temperature with a rotor speed of 50 rpm. The ENR or NBR was charged first into the mixing chamber, then stearic acid, Ca(OH)_2 , TAIC and DBPH were added, respectively. Mixing was then continued until a constant torque was obtained. The total mixing time was 10 minutes. The compound was removed from the mixer and was tested in next steps. The formulations were shown in table 3.1.

Table 3.1 Formulations of rubber blends for curing characterization

Materials	Quantity, phr ^a	Mixing times, min
ENR or NBR	100	0 - 2
Stearic acid	0.25	2 - 3
Ca(OH)_2	3	3 - 6
TAIC	X/2	6 - 8
DBPH	X	8 - 10

Note: ^aphr is part per hundred part of rubber and X is the varying DBPH content at 3, 5 and 7 phr.

3.2.2 Preparation of Thermoplastic Parts

The thermoplastic parts which contain PVDF, triacetin (5 phr) and PLA, if any, were prepared by melt-mixing in a co-rotating twin screw extruder (LTE20-40 model). In case of adding PLA, the PVDF/PLA blends were mixed at composition of 80/20. The temperature profile from the feed zone to die is 175, 180, 185, 185, 190, 190, 195, 195, 200, 210 °C. The screw speed was used at 50 rpm. The extrudate was cooled in water bath and then cut into pellet by pelletizer.

3.2.3 Preparation of Thermoplastic Vulcanizate (TPV)

The formulations of the TPV blends are given in Table 3.2. First step, the rubber parts were prepared at room temperature by using two roll mill (LRM 110 model). The ENR or NBR was mixed with stearic acid, Ca(OH)₂, organoclay, if any, TAIC, DBPH and triacetin, respectively. The total mixing time was 45 min. The compound was removed from two roll mill, cut it to be small strips, put thermoplastic blends pellets which obtained from 3.2.2 on top of rubber compound surface and fed in twin screw extruder, respectively.

Last step, the TPV was achieved by blending thermoplastic and rubber via twin screw extruder by using temperature profile from the feed zone to die of 185, 188, 188, 178, 180, 182, 185, 188, 190, 190 °C. The screw speed was used at 70 rpm. Then the extrudate was cooled in water bath and then cut into pellets by pelletizer.

The formulations of the TPV blends with organoclay and TPV blends of NBR are given in Table 3.3 and 3.4, respectively. The TPV blends pellets were compressed in a compression mold (Wabash MPI, V50H-18-CX model, USA). Hot-press procedures involved pre-heating at 190 °C for 5 min, followed by compressing for 5 min at the same temperature with pressure of 20 tons.

Table 3.2 Formulations of TPV blends

Materials	Blends (wt %)					
	I	II	III	VI	VII	VIII
ENR	50	60	70	50	60	70
PVDF	40	30	20	50	40	30
PLA	10	10	10	-	-	-
DBPH ^a	X	3	3	X	3	3
TAIC ^a	X/2	1.5	1.5	X/2	1.5	1.5
Stearic acid ^a	0.25	0.25	0.25	0.25	0.25	0.25
Ca(OH) ₂ ^a	3	3	3	3	3	3
Triacetin ^a	2.5	2.5	2.5	2.5	2.5	2.5
Triacetin ^b	2.5	2.5	2.5	2.5	2.5	2.5

Note: X is the varying DBPH content at 3, 5 and 7 phr, ^a At phr of rubber and ^b At phr of plastic. A similar ternary blends of ENR/PVDF with PLA were prepared but without the addition of DBPH, TAIC, Stearic acid and Ca(OH)₂.

3.3 Characterizations

3.3.1 Curing Characteristics of Rubber Parts

The curing properties of rubber parts including curing rate, curing time and the practical curing temperature in DBPH system were observed by using MDR and DSC before moving to a compression step.

For MDR (rheoTECH MD+, Tech pro, A022S), they were tested under operation of constant conditions (0.5 deg arc strain amplitude, rotor size L) at various temperatures ranging from 180 – 200 °C. For DSC (DSC822E model, Mettler Toledo), they were characterized under nitrogen atmosphere with a flow rate of 10 ml/min. All of samples were heated at 180, 190 and 200 °C for 30 minutes in case of isothermal method and were heated from 30 °C to 300 °C with the heating rate of 10 °C/min in case of non-isothermal method.

Table 3.3 Formulations of organoclay-filled TPV blends

Materials	Blends (wt %)	
	I	II
ENR	50	50
PVDF	40	50
PLA	10	-
DBPH ^a	5	5
TAIC ^a	2.5	2.5
Stearic acid ^a	0.25	0.25
Ca(OH) ₂ ^a	3	3
Organoclay ^a	X	X
Triacetin ^a	2.5	2.5
Triacetin ^b	2.5	2.5

Note: X is the varying organoclay content at 0, 3, 5, 7 and 10 phr, ^a At phr of rubber and ^b At phr of plastic.

Table 3.4 Formulations of TPV blends of NBR

Materials	Blends (wt %)	
	I	II
ENR or NBR	50	50
PVDF	40	50
PLA	10	-
DBPH ^a	5	5
TAIC ^a	2.5	2.5
Stearic acid ^a	0.25	0.25
Ca(OH) ₂ ^a	3	3
Triacetin ^a	2.5	2.5
Triacetin ^b	2.5	2.5

3.3.2 Rheological Properties

The viscosity of ENR, NBR, PVDF and PVDF/PLA blends were measured by using rheometer (ceast 5000 model) at 180, 185, 188 and 190 °C. The L/D ratio of used die was 20/1. The shear rates were determined from 40 to 6,000 (1/s).

3.3.3 Thermal Properties of TPV Blends after Twin Screw Extruder

The thermal properties of TPV blends obtained from twin screw extruder were analyzed using DSC (DSC822E model, Mettler Toledo) and compared with thermograms of PVDF and PVDF/PLA blend. The samples were tested under nitrogen atmosphere with a flow rate of 10 ml/min and heated from 30 °C to 200 °C with the heating rate of 10 °C/min and held for 3 minutes to delete a thermal history. Then, they were cooled down to 30 °C and re-heated again to 200 °C at the same rate. The melting temperature and cold crystallization temperature were obtained from DSC thermograms. The relative percent crystallinity of PVDF and PVDF/PLA blends at the composition of 80/20; X_{BLEND} (%) were calculated according to the equation 3.1 and 3.2, respectively. The TPV with 10 % of PLA at the rubber/thermoplastic composition of 50:50 ratio was calculated according to the equation 3.3:

$$X_{\text{PVDF}} (\%) = \frac{\Delta H^*_{\text{PVDF}}}{\Delta H^0_{\text{PVDF}}} \times 100 \quad (3.1)$$

$$X_{\text{BLEND}} (\%) = \frac{\Delta H^*_{\text{BLEND}}}{(0.8 \times \Delta H^0_{\text{PVDF}}) + (0.2 \times \Delta H^0_{\text{PLA}})} \times 100 \quad (3.2)$$

$$X_{\text{TPV}} (\%) = \frac{\Delta H^*_{\text{TPV}}}{(0.4 \times \Delta H^0_{\text{PVDF}}) + (0.1 \times \Delta H^0_{\text{PLA}})} \times 100 \quad (3.3)$$

Next, the TPV blends were studied using MDR (rheoTECH MD+, Tech pro, A022S), they were tested under operation of constant conditions (0.5 deg arc strain amplitude, rotor size L) at various temperatures ranging from 180 – 200 °C.

3.3.4 Mechanical Tests

The mechanical properties including the tensile strength, tear strength and hardness (shore A). Tensile test was done according to ASTM D412-06a or ISO 37 (type 1), tear test was done according to ASTM D624-00 or ISO 34 by using the universal testing machine (Instron, 4206-006 model) with load cell of 5 kN and crosshead speed of 500 mm/min. The hardness was determined according to ASTM D2240 by using shore A durometer (Zwick, type 7206). Five specimens were used in each case.

3.3.5 Thermal Properties of TPV Blends after Compression

Thermal properties of TPV samples after compression were characterized by using DSC (DSC822E model, Mettler Toledo) operated under nitrogen atmosphere with a flow rate of 10 ml/min. All of samples were heated from 30 °C to 200 °C with the heating rate of 10 °C/min and held for 3 minutes to delete a thermal history. Then, they were cooled down to 30 °C and re-heated again to 200 °C at the same rate. The second heat was reported as heating curve. The melting temperature and cold crystallization temperature were obtained from DSC thermograms. The relative percent crystallinity of PVDF and PVDF/PLA thermoplastic blends at the composition of 80PVDF/20PLA; X_{BLEND} (%) were calculated according to the equation 3.1 and 3.2, respectively. TPV with 10 % of PLA and TPV without PLA at the rubber/thermoplastic composition on 50:50 ratio were calculated according to the equation 3.3 and 3.4, respectively. TPV with 10 % of PLA and TPV without PLA at the rubber/thermoplastic composition on 70:30 ratio were calculated according to the equation 3.5 and 3.6, respectively:

$$X_{\text{PVDF}} (\%) = \frac{\Delta H^*_{\text{PVDF}}}{\Delta H^0_{\text{PVDF}}} \times 100 \quad (3.1)$$

$$X_{\text{BLEND}} (\%) = \frac{\Delta H^*_{\text{BLEND}}}{(0.8 \times \Delta H^0_{\text{PVDF}}) + (0.2 \times \Delta H^0_{\text{PLA}})} \times 100 \quad (3.2)$$

$$X_{\text{TPV}} (\%) = \frac{\Delta H^*_{\text{TPV}}}{(0.4 \times \Delta H^0_{\text{PVDF}}) + (0.1 \times \Delta H^0_{\text{PLA}})} \times 100 \quad (3.3)$$

$$X_{\text{TPV}} (\%) = \frac{\Delta H^*_{\text{TPV}}}{(0.5 \times \Delta H^0_{\text{PVDF}})} \times 100 \quad (3.4)$$

$$X_{\text{TPV}} (\%) = \frac{\Delta H^*_{\text{TPV}}}{(0.2 \times \Delta H^0_{\text{PVDF}}) + (0.1 \times \Delta H^0_{\text{PLA}})} \times 100 \quad (3.5)$$

$$X_{\text{TPV}} (\%) = \frac{\Delta H^*_{\text{TPV}}}{(0.3 \times \Delta H^0_{\text{PVDF}})} \times 100 \quad (3.6)$$

While, ΔH^* is the measured enthalpy of PVDF or PLA. ΔH^0 is the enthalpy of melting per gram of 100 % crystalline, 93 J/g for PLA (P. Boonfuang *et al.*, 2011) and 104.7 J/g for PVDF (Marega C. *et al.*, 2003). And percent crystallinity of the blends was calculated from the combination of the enthalpy of melting per gram of 100 % crystalline (ΔH^0) of PVDF and PLA.

3.3.6 Dynamic Mechanical Analyzer (DMA)

The storage modulus (E'), the loss modulus (E''), and the dissipation factor ($\tan \delta$) are measured by DMA (GABO-EPLEXOR 100N model) using a constant frequency of 1 Hz and a temperature range of -80°C to $+120^\circ\text{C}$. The measurements were carried out under tension mode with a static load of 10 N and a dynamic load of 5 N. The dimensions of the test samples were in width*length*thickness (10*2 mm).

3.3.7 Oil Swelling Test

The oil resistance of the blends was studied after immersing sample in oil at temperature of 25°C and 100°C for 24 hours and 7 days according to ASTM D471-06 or ISO 2285 (Method A). In this study, gasohol 91, gasohol 95, E20 and E85 which contain 10, 10, 20 and 85 % ethanol, respectively, were used. After removal from the oil, the test pieces were wiped with tissue paper to remove excess oil from the surface and weighed immediately. The swelling index and percentage of swelling were calculated using equation 3.7 and 3.8, respectively:

$$\text{Swelling index} = \frac{\text{Final mass}}{\text{Initial mass}} \quad (3.7)$$

$$\% \textit{Swelling} = \frac{W_s - W_o}{W_o} \times 10 \quad (3.8)$$

Note: Where W_s refer to a swelling weight and W_o refer to an original weight.

3.3.8 Morphology Characterization

The morphology of rubber and plastic phases, the vulcanized rubber particles size and the dispersion of vulcanized rubber particles was examined by using the field emission scanning electron microscope (FE-SEM) HITACHI S-4800 model which contributed the images in the magnification range of 1,000 to 10,000 times at 10 kV. The samples must be coated with platinum under vacuum condition before observation to make them electrically conductive.