



## CHAPTER III METHODOLOGY

### 3.1 Materials and Equipment

#### 3.1.1 Materials

Natural Rubber (Banpan Research Laboratory Co., Ltd), poly(Vinylidene Fluoride) (PVDF) (Assembly Chemicals Co., Ltd), poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) (Thantawan Industry PCL.), 2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane (Luperox<sup>®</sup> 101 or DBPH) (Sigma-Aldrich Co.), dicumyl peroxide (DCP) (Sigma-Aldrich Co.), N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS) (Inoue Rubber Thailand PCL.), zinc oxide (ZnO) (Inoue Rubber Thailand PCL.), steric acid (Neoplastomer Co., Ltd.), sulfur (Banpan Research Laboratory Co., Ltd.), calcium hydroxide (Fluka Chemical Corp.), triallyl isocyanurate (TAIC<sup>®</sup>) (Neoplastomer Co., Ltd.), gasohol 91, 95, E20, E85 and biodiesel B5 (PTT PCL.).

#### 3.1.2 Equipment

##### 3.1.2.1 *Internal Mixer*

An internal mixer was a Brabender Plasti-corder 815602 type. It was manufactured by Brabender<sup>®</sup> 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 *Twin-Screw Extruder*

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

##### 3.1.2.3 *Cooling Bath*

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

#### *3.1.2.4 Pelletizer*

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

#### *3.1.2.5 Two-Roll Mill*

An open-mixer, two-roll mill, was manufactured by Labtech Engineering Co., Ltd (Bangkok, Thailand). It was a LRM 110 model with a capacity of 200 g.

#### *3.1.2.6 Compression Mold*

The compression mold was a V50H-18-CX model with a compress capacity of 50 ton. It 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 with a temperature range of 100–200 °C. It was supplied by CG Engineering Ltd., Part.

#### *3.1.2.8 Differential Scanning calorimeter (DSC)*

The Perkin-Elmer DSC 7 was used to determine the melting temperature ( $T_m$ ) and percent crystallinity under a  $N_2$  atmosphere with a flow rate of 10 ml/min.

#### *3.1.2.9 Pneumatic Punch*

The pneumatic punch was use to cut specimens from vulcanized sheet into dumbbell shape incorporated with die C according to ASTM D3183.

#### *3.1.2.10 Universal testing machine (Instron)*

A Universal Testing Machine (Instron) was a 4206-006 model. It was used to measure the tensile strength, percent elongation at break, Young's modulus, and tear strength. It equipped with a 5 kN load cell was used to measure mechanical properties in tension. The specimens were loaded at a rate of 500 mm/min. Specimens of 25 mm gauge length and 2 mm thick were used for tested of each thermoplastic vulcanizates. The specimens were loaded until break.

#### *3.1.2.11 Durometer*

A durometer is a Zwick, 7206 type. It was used to determine the hardness of samples according to ASTM D2240 in shore A.

#### 3.1.2.12 Air Oven

An air oven was used for aging test in order to accelerate the age of specimens. The accelerated test was done at the temperature of 100 °C for 22 h according to ASTM D 573 – 04. The aged specimens were sequentially measured the tensile strength, elongation at break and tear strength within 96 h after started aging.

#### 3.1.2.13 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) will be performed on HITASHI S-4800 Model to examine phase morphology of thermoplastic vulcanizates. The samples were coated with platinum under vacuum before observation to make them electrically conductive. All SEM images will be obtained in the magnification range of 500 to 5000 times at 15 kV.

### 3.2 Methodology

#### 3.2.1 Preparation of Natural Rubber

The compounded NR was derived from compounding NR (STR 5L grade) with chemicals for any vulcanization system in an internal mixer (Brabender<sup>®</sup> Plasticorder, 815602 type, Germany). The efficient vulcanization system (EV system) used the Acc:S ratio of 12, steric acid and zinc oxide (ZnO) were used as activators, N-Cyclohexyl-2-Benzothiazyl Sulfenamide (CBS) was used as an accelerator, and sulfur was used as a vulcanizing agent. For the system involving peroxide, dicumyl peroxide (DCP) and 2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane (Luperox<sup>®</sup> 101 or DBPH) were used as peroxide vulcanizing agents. The formula of DBPH system was adopted from Magaraphan *et al.*, 2008. Calcium hydroxide (Ca(OH)<sub>2</sub>) was used as activator. Triallyl Isocyanurate (TAIC<sup>®</sup>) was used as a coagent. The quantity of DBPH was also varied as 3, 5, and 7 phr. The formulae and mixing schedule are given in Table 3.1.

**Table 3.1** Compounding formulae and mixing schedule

Ingredients	EV system		DCP system		DBPH system	
	Quantity (phr <sup>a</sup> )	Mixing time (min)	Quantity (phr <sup>a</sup> )	Mixing time (min)	Quantity (phr <sup>a</sup> )	Mixing time (min)
NR	100	5	100	5	100	4
Steric acid	1	1	-	-	0.25	1
ZnO	5	1	-	-	-	-
CBS	6	1	-	-	-	-
Sulfur	0.5	4	-	-	-	-
DCP	-	-	3	7		
Ca(OH) <sub>2</sub>	-	-	-	-	3	1
TAIC	-	-	-	-	3	2
DBPH	-	-	-	-	3 <sup>b</sup>	4

<sup>a</sup>phr = part per hundred part of rubber.

<sup>b</sup>The amount of DBPH was varied by 3, 5, and 7 phr.

The mixing was performed at room temperature with a rotor speed of 80 rpm. After mixing, the blend was then removed from the internal mixer and later mixed and masticated into the sheet form by using a two-roll mill (Labtech, LRM 110 model, Thailand). Then, the sheet compounded NR was further compressed in a compression mold (Wabash MPI, V50H-18-CX model, USA) at the temperature of 150 °C for sulfur system and 180 °C for peroxide system using 20 ton force of pressure for 10 min. The vulcanized NRs of various vulcanization systems were obtained.

### 3.2.2 Preparation of NR/PVDF Thermoplastic Vulcanizate

The thermoplastic vulcanizate was achieved by blending thermoplastic and elastomeric materials together via the dynamic vulcanization technique. NR was blended with PVDF at the fixed composition of 50/50 in an

internal mixer (Brabender<sup>®</sup> Plasticorder, 815602 type, Germany) at various vulcanization systems according to the formulae and mixing schedule given in Table 3.2.

**Table 3.2** Compounding formulae and mixing schedule

Ingredients	CV system		EV system		Peroxide system	
	Quantity (phr <sup>a</sup> )	Mixing time (min)	Quantity (phr <sup>a</sup> )	Mixing time (min)	Quantity (phr <sup>a</sup> )	Mixing time (min)
PVDF	50	5	50	5	50	5
NR	50	5	50	5	50	5
Steric acid	2	1	2	1	0.125	1
ZnO	3.5	1	3.5	1	-	-
CBS	0.9	2	3	2	-	-
Sulfur	1.8	2	1.5	2	-	-
Ca(OH) <sub>2</sub>	-	-	-	-	1.5	1
TAIC	-	-	-	-	1.5	2
DBPH	-	-	-	-	Varied <sup>b</sup>	1

<sup>a</sup>phr = part per hundred part of rubber.

<sup>b</sup>The amount of DBPH was varied by 1, 3, 5, and 7 phr, which were calculated from NR 100 phr.

For the system involving sulfur (the formulae was adopted from Boochathum *et al.*, 2001), the Acc:S ratio were used at 0.5 and 2.0 for the CV and EV systems, respectively. In peroxide system (the formulae was adopted from Magaraphan *et al.*, 2008, 2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane (Luperox<sup>®</sup> 101 or DBPH) was used as a peroxide vulcanizing agent and the quantity of DBPH was varied at 1, 3, 5, and 7 phr. Mixing was performed at a rotor speed of 80 rpm at the temperature of 150 °C. Mixing was done until the vulcanization of NR was

started to occur indicated the increasing torque curve. The blend was then removed from the internal mixer and later mixed and masticated into the sheet form by using a two-roll mill (Labtech, LRM 110 model, Thailand) and obtained a pre-vulcanized TPV. This pre-vulcanized TPV was fully vulcanized by further compressing in a compression mold (Wabash MPI, V50H-18-CX model, USA) with the pressure of 20 ton force at the temperature of 150 °C for sulfur system and 180 °C for peroxide system for 10 min. Then cooled down and the TPV was obtained.

### 3.2.3. Preparation of PVDF/PHBV Blend

PVDF and PHBV were first mix together with a PVDF/PHBV composition of 80/20 by using a co-rotating twin-screw extruder (Labtech, LTE20-40 model, Thailand) to obtain a PVDF/PHBV blend. The temperature profile from the feed zone to die is 160, 170, 180, 180, 185, 190, 195, 200, 205, 210. The screw speed was used at 50 rpm with the pressure of 60 bar. The extrudate was cooled in the water bath (Labtech LW-100 model) and then cut into pellet by pelletizer (Labtech, LSC-108 model).

### 3.2.4 Preparation of NR/PVDF/PHBV Thermoplastic Vulcanizate

The thermoplastic vulcanizate was achieved by blending thermoplastic and elastomeric materials together via the dynamic vulcanization technique. NR was blended with PVDF and PHBV at the fixed composition of 50NR/40PVDF/10PHBV. NR was separately mixed with chemicals by using an internal mixer (Brabender<sup>®</sup> Plasticorder, 815602 type, Germany) at room temperature. In this study, epoxidized soybean oil (ESO) was added in the mixture by varying content 0, 1, 2, 5, 7, and 10 phr (calculated from NR 100 phr). Half of ESO was added to NR in the compounding process and another half was added in mixing compounded NR with thermoplastic blend. The formula and schedule for compounding NR is given in Table 3.3. The formula was adopted from Magaraphan, *et al.*, 2008. 2,5-Bis(Tert-Butylperoxy)-2,5-Dimethylhexane (DBPH or Luperox<sup>®</sup> 101) was used as a peroxide vulcanizing agent. The compounding of NR was performed at a rotor speed of 80 rpm at room temperature without adding curing agent and remove at the end of mixing time.

**Table 3.3** Formula and mixing schedule for compounding NR

Ingredients	Quantity (phr <sup>a</sup> )	Mixing time (min)
NR	100	-04
ESO	Varied <sup>b</sup>	4-6
Steric acid	0.125	6-7
Ca(OH) <sub>2</sub>	1.5	7-8
TAIC	1.5	8-10

<sup>a</sup>phr = part per hundred part of rubber.

<sup>b</sup>The amount of ESO was varied by 0, 1, 2, 5, 7, and 10 phr which were calculated from NR 100 phr and were added in a half in compounding NR.

After that, the 80/20 % by weight of PVDF/PHBV blend was incorporate with compounded NR in the composition of 50/50 at 150 °C according to the mixing schedule as shown in Table 3.4. The composition of TPV contained 3 materials of NR/PVDF/PHBV is 50/40/10.

**Table 3.4** Schedule for mixing compounded NR and thermoplastic blend

Ingredients	Quantity (phr <sup>a</sup> )	Mixing time (min)
PVDF/PHBV blend	50	0-5 or plateau torque reached
Compounded NR	50	5-8 or plateau torque reached
ESO	Varied <sup>b</sup>	8-10 or plateau torque reached
DBPH	3	10-11 or the torque started to increase

<sup>a</sup>phr = part per hundred part of rubber.

<sup>b</sup>The amount of ESO was varied by 0, 1, 2, 5, 7, and 10 phr which were calculated from NR 100 phr and were added in a half in mixing the compounded NR with PVDF/PHBV blend.

The mixing was done until the vulcanization of NR was started to occur indicated in the plateau torque of well mixing was started to increase again to obtain the pre-vulcanized TPV. Next, it was then removed from the internal mixer and later mixed and masticated into the sheet form by using a two-roll mill (Labtech, LRM 110 model, Thailand). This pre-vulcanized TPV was fully vulcanized by further compressing in a compression mold (Wabash MPI, V50H-18-CX model, USA) at the temperature of 180 °C with the pressure of 20 ton force for 10 min. Then the TPV was obtained after cooling down.

### 3.3 Characterization

#### 3.3.1 Cure Characteristic and Vulcanization Parameters

The cure characteristic and vulcanization parameter of compounded NR was first determined by using Moving Die Rheometer (MDR) before compress in a compression mold. All vulcanization systems, EV, DCP, and DBPH, were characterized by varying the temperature from 150 °C to 200 °C. The sulfur systems of compounded NR, CV and EV system, were also characterized compared between the temperature of 150 °C and 180 °C. The NR/PVDF thermoplastic vulcanized was characterized by varying the DBPH contents at the temperature of 180 °C. The NR/PVDF/PHBV thermoplastic vulcanizates was characterized by varying the amount of ESO added at the 180 °C in DBPH system.

#### 3.3.2 Characterization of Thermal Properties of PVDF/PHBV Blend

PVDF/PHBV blend was characterized thermal properties by using a differential scanning calorimeter (DSC) (Perkin-Elmer, DSC 7) operated under a N<sub>2</sub> atmosphere with a flow rate of 10 ml/min. The sample was heated from -20 °C to 200 °C with the heating rate of 10 °C/min and held for 3 min to destroy a thermal history. Then, they were cooled down to -20 °C and re-heated to 200 °C again at the same rate. Their thermal properties were obtained. The crystallinity percentage ( $X_c$ ) of PVDF and PHBV were calculated by Equation 3.1:

$$X_c(\%) = \frac{\Delta H^*}{\Delta H^0} \times 100 \quad , \quad (3.1)$$



$\Delta H^*$  is the measured enthalpy of PVDF or PHBV.  $\Delta H^0$  is the enthalpy of melting per gram of 100 % crystalline, 109 J/g for PHBV, and 104.7 J/g for PVDF. And percent crystallinity of the blend was calculated from the combination of the enthalpy of melting per gram of 100 % crystalline ( $\Delta H^0$ ) of PVDF and PHBV at the composition of 80PVDF/20PHBV according to the Equation 3.2:

$$X_{c,Blend}(\%) = \frac{\Delta H_{Blend}^*}{(0.8\Delta H_{PVDF}^0 - 0.2\Delta H_{PHBV}^0)} \times 100 . \quad (3.2)$$

### 3.3.3 Study of Thermal Properties of NR/PVDF/PHBV Thermoplastic Vulcanizates

Thermal properties of TPVs at various amount of ESO were characterized by using a differential scanning calorimeter (DSC) (Perkin-Elmer, DSC 7) operated under a N<sub>2</sub> atmosphere with a flow rate of 10 ml/min like PVDF/PHBV blend. All of samples were heated from 30 °C to 200 °C with the heating rate of 10 °C/min and held for 3 min to destroy 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 of ESO varied TPV were obtained from DSC thermograms. The crystallization was occurred from PVDF and PHBV, so percent crystallinity of TPVs were determined from Equation 3.3:

$$X_{c,TPV}(\%) = \frac{\Delta H_{TPV}^*}{(0.4\Delta H_{PVDF}^0 - 0.1\Delta H_{PHBV}^0)} \times 100 . \quad (3.3)$$

While,  $\Delta H^*$  is the measured enthalpy of PVDF or PHBV.  $\Delta H^0$  is the enthalpy of melting per gram of 100 % crystalline, 109 J/g for PHBV, and 104.7 J/g for PVDF. And percent crystallinity of the blend was calculated from the combination of the enthalpy of melting per gram of 100 % crystalline ( $\Delta H^0$ ) of PVDF and PHBV at the composition of 40PVDF/10PHBV.

### 3.3.4 Study of Mechanical Properties

The mechanical properties in this study were tensile strength, percent elongation at break, and Young's modulus, tear strength, and hardness. The universal testing machine (Instron, 4206-006 model) with a load cell of 5 kN and the crosshead speed of 500 mm/min was used to determine the tensile strength, percent elongation at break, and Young's modulus according to ASTM D412-06a or ISO 37 (Type 1) and determine the tear strength was determined according to ASTM D624-00 or ISO 34. These mechanical properties were also done after aging at 100 °C for 22 h in air

oven followed ASTM D573-04 for NR/PVDF TPV. The hardness was determined according to ASTM D2240 by using a durometer (Zwick, type 7206) shore A.

### 3.3.5 Study of Swelling Resistance

The Swelling test was done at temperature of 25 °C and 100 °C for 24 hours and 7 days according to ASTM D471-06 or ISO 2285 (Method A). Biodiesel oil with 5 % biodiesel which was called B5 and gasohols with 10 %, 20 %, and 85 % ethanol, which were called 91, 95, E20, and E85, were used as the test liquids. The increase in degree of swelling in percent by weight was calculated as the following Equation 3.4:

$$\% \text{ Swelling} = \frac{(W_s - W_o)}{W_o} \times 100 \quad , \quad (3.4)$$

and the swelling index was also determined from Equation 3.5:

$$\text{Swelling Index} = \frac{W_s}{W_o} \quad , \quad (3.5)$$

where the  $W_s$  refer to a swelling weight, and the  $W_o$  refer to an original weight.