



CHAPTER III

EXPERIMENTAL

3.1 Raw Material

Reagent	Trademane	Manufacture
Ethylene-Vinylacetate	C-I-L 1710	ICI
Polyisoprene Rubber	NAT SYN 2200	Goodyear
Precipitated Silica	Hoesch KS404	Azo Chemie
Coated Calcium Carbonate	SCC-2T	Silathip Chemie
Stearic Acid	-	Siam Oil
Zinc Oxide (active)	Zinkoxyd aktiv	Bayer
Dicumyl Peroxide	Percumyl D	Nippon Oil & Fat Co.,LTD
Zinc Stearate	-	Nippon Kokaku Chemical
Blowing Agent	AK#2	EIWA
Natural Rubber	ADS.	Thailand

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3.2 Machine and Equipment

Internal Mixer (Appendix A):

- Capacity 420 g
- Rotor speed 0-120 rpm
- Specific ram pressure 0-4 bar
- Temperature 30 - 300 °C
- Cooling by Air and water

Two Roll Mill (Appendix A):

- Roll diameter * length 10 * 25 cm
- Rotor speed 24 rpm
- Friction ratio 1 : 1.14
- Temperature 30-120 °C
- Cooling by Air

Hot Press (Appendix C):

- Ram diameter 17 cm
- Size of heat plate 40*40 cm²
- Maximum pressure 200 kg/cm²
- Heating electric heater

Gas Measurement Apparatus (Appendix B)

Mold size : 12 * 12 * 1 cm³

Rheometer (Appendix C) : Monsanto U.S.A

Processability Tester (Appendix D) : Monsanto U.S.A

Universal Testing Instrument(Appendix D):Instron U.S.A

Microscope : ZEISS West German

Table 3.1 The experimental formulation (by phr)

Formulation No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Reagent													
EVA Copolymer	100	100	100	100	100	100	100	95	90	85	95	90	85
Polyisoprene	0	0	0	0	0	0	0	5	10	15	0	0	0
Natural Rubber	0	0	0	0	0	0	0	0	0	0	5	10	15
Precipitated Silica	10	10	10	10	10	10	10	10	10	10	10	10	10
Calcium Carbonate	6	6	6	6	6	6	6	6	6	6	6	6	6
Stearic Acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zinc Stearate	1	1	1	1	1	1	1	1	1	1	1	1	1
Zinc Oxide	0	0	0	0	0	0.4	1	0	0	0	0	0	0
Blowing agent	2.5	5	8	5	5	5	5	5	5	5	5	5	5
Cross-linking agent	0.8	0.8	0.8	0.6	1.2	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8

Unit : Phr (Part per Hundred Rubber)

Table 3.2 The experimental formulation (by weight)

Formulation No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Reagent													
EVA Copolymer	350	350	350	350	350	350	350	332.5	315	297.5	332.5	315	297.5
Polyisoprene	0	0	0	0	0	0	0	17.5	35	52.5	0	0	0
Natural Rubber	0	0	0	0	0	0	0	0	0	0	17.5	35	52.5
Precipitated Silica	35	35	35	35	35	35	35	35	35	35	35	35	35
Calcium Carbonate	21	21	21	21	21	21	21	21	21	21	21	21	21
Stearic Acid	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
Zinc Stearate	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Zinc Oxide	0	0	0	0	0	0	1.4	3.5	0	0	0	0	0
Blowing agent	8.75	17.5	28	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5	17.5
Cross-linking agent	2.8	2.8	2.8	2.1	4.2	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8

Unit:Gram

Table 3.3 Basic process and condition of EVA foaming

Measuring	Compounding			Storage Stage	Cross-linking/ Foaming	Sample Analysis
	Stage1	Stage2	Stage3			
-EVA Copolymer -Polyisoprene Rubber -Ingredients	All ingredients and polymer except AK#2 and DCP Internal Mixer: -Temp. 90-110 °C -Ram Pressure 4 bar -Rotor Speed 63 rpm	Add AK#2 and DCP	Two roll mill: -Nip 1 mm -Temp. 92 °C	air: Temp. 30-35°C	Hot Press : -Ram pressure 150 bar -Temp. 165,185 °C	

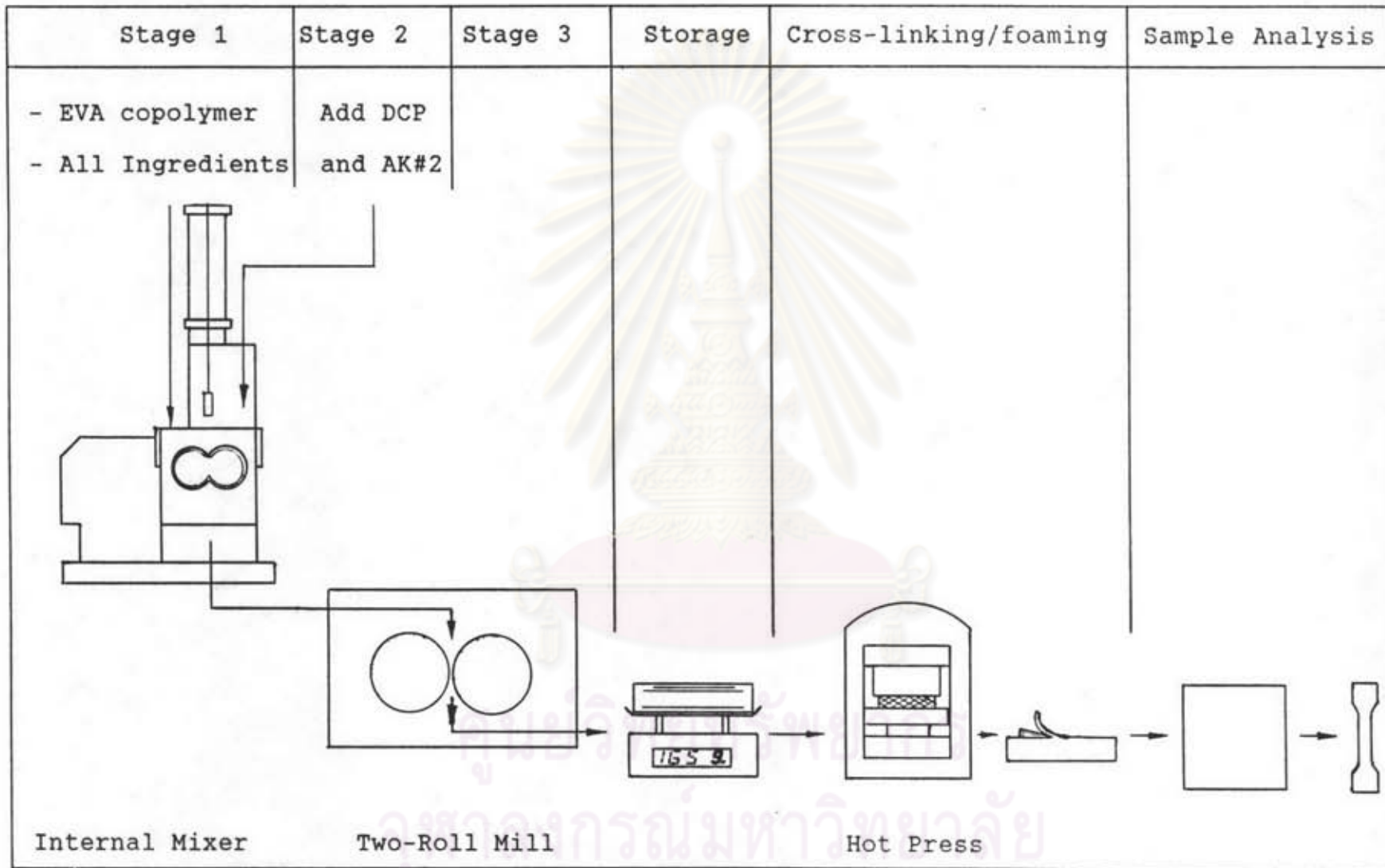


Figure 3.1 The flow diagram of EVA foaming process

3.3 Investigation Steps

The investigation steps can be divided in to several parts as followed:

3.3.1 Formulation

The commercial formulations for shoe soles are shown in Table 3.1. Only one grade of commercial EVA copolymer was used with a vinylacetate content of 17 percents, an melt flow index (MFI) value of 1.5 and a viscous softening point of 63 °C. Also one grade of cis 1,4 polyisoprene (IR 2200) with mooney viscosity, ML 1+ 4(100 °C) 80 +10 was used and a natural rubber (ADS grade which mooney viscosity, ML 1+4(100°C) 74) was also used in compounding.

One type of modified azodicarbonamide (6) (average particle size 8 µm, decomposition temperature range of 118-124°C, and generate gas volume of 125 ml/g) was used. Dicumyl peroxide (98 percents active) was used as cross-linking agent. The amount of dicumyl peroxide (7) was varied from 0.8 to 1.2 phr(part per hundred rubber) which represents the recommended value for EVA foams for improved permanent set.

Two processing aids which normally used to improve filler dispersion (5) were used in the formulations : zinc stearate and stearic acid. Mainly precipitated silica and coated calcium carbonate which

used at fix level were compounded as filler. Zinc oxide (8) may be added as an activator of blowing agent and also acted as nucleating agents, giving a cell structure of uniform fineness.

For a better understanding, the formulations which shown in Table 3.1 can be devided in two main basic group as followed:

1) EVA group (Formulation No.1-No.7).

This group used only EVA copolymer in the formulations which will be used as a basic formulation for investigation to find out the optimun condition in EVA foaming process. The results that obtain in these observations will also used as a basic information for the next steps.

2) EVA and polyisoprene group (Formulation No.8-No.13) is another group that EVA copolymer and synthetic polyisoprene rubber or natural rubber were use to investigate the replacement of synthetic polyisoprene by natural rubber in the foaming proecss.

3.3.2 Sample Preparation

The sample preparation procedure was shown in Figure 3.1 and also the preparation conditions were summerized in the Table 3.3 this sample preparation can also well understand by follownig details.

1) Weight : EVA copolymer and other ingredients were measured according to the formulations in Table 3.1 with the total weight of 420 gram/batch (Table 3.2)

2) Compounding stage 1 : EVA copolymer and other ingredients except blowing and cross-linking agent were compounded in the interal mixer untill the uniform mixture was obtained. The temperature in the mixer was controlled between the softening point of the compound ($90-92^{\circ}\text{C}$) and below the decomposition temperature of both blowing agent (118°C) and cross-linking agent (110°). The reason of fixing this temperature rage is the fact that the decomposition of the blowing agent (6) and the activity of cross-linking agent to vulcanization, the compound may be scroched and lost some gases (9). The ram pressure (4bar), rotor speed (63 rpm) and various compounding time were chosed for study.

3) Compounding stage 2 : The blowing agent and cross-linking agent were added in the mixer and compounded untill the mixture became uniform yellow. The temperature and other conditions were controlled as same as in compounding stage 1.

4) Compounding stage 3 : After the compounding stage 2 was completed, immediately transfer the mixture sample into a two-roll mill. The two-roll

used for sheeting or ultimate mixing of a blowing agent and a cross-linking agent. The temperature of the rolls was fixed at 92°C because of softening point of EVA compound. The nip and compounding time also related to the degree of mixing(2). The nip was fixed at 1 millimeter. for this investigation because this length is an efficient nip for the good mixing.

5) Storage stage : After the compounding stage had been completed, the mixture sample was stored by placing in air at room temperature (30-35°) for several storage time and the sample was cut to the size (11 * 11 cm²) smaller than the mold size.

6) Cross-linking/foaming stage : The sample was weighed (165 g) to more than 3 percents of the mold volume (5) and filled to the mold (to seal the mold). The mold was closed by the hot press with pressure of 150 kg/cm² (6). The recommend cure temperatures were 165°C and 185°C. Several cure time were used also to study the cross-linking/foaming process of EVA compound (5,7,8,9). After the suitable cure time, the mold was immediately opened and the expansion of EVA foam took place in less than two seconds. The sample was analysed by follow the methods as in 3.4.

3.3.3 Investigation Process Parameters

The following parameters which also play as the preparation factors are selected for this observation.

- compounding stages
- storage stage
- Cure Time/Temperature in the cross-linking/foaming stage

1) Compounding Stages

The compounding stages which are investigated can be separated into three stages

a) Compounding stage 1. All active ingredients except a blowing agent and cross linking agent(as shown in formulation NO.1-NO.7) were compounded into the internal mixer using compounding condition as described in 3.3.2. The compounding time was varied range from 10 - 35 minutes. The shear viscosity of the sample was analysed by using the processability tester(detail in 3.4).

b) Compounding stage 2. This stage was an addition of blowing and cross-linking agent to a previous compounding in the internal mixer. In this stage, again compounding time was varied between 2 and 15 minutes. The foaming and cross-linking of the sample were analysed by using a gas measurement apparatus and rheometer (detail in 3.4).

c) Compounding stage 3. After the compounding stage 2 was completed, immediately transferred the compounding sample into the two-roll mill, mixing condition as in 3.3.2. The compounding time in this two-roll mill was observed starting from single sheeting up to 15 minutes sheeting time. The foaming and cross-linking of the sample were analysed by using gas measurement apparatus and rheometer (detail in 3.4).

The variation in the above compound stages was summarized in the following Table.

Table 3.4 Variation time in compounding stage

Formulation No.	Compounding time		
	Stage 1	Stage 2	Stage 3
No. 1-No. 5	10-35 min.		
No. 1-No. 7	Optimum Condition*	2-15 min.	
No. 1-No. 7		Optimum Condition*	0-15 min.

*Optimum condition of each stage will be selected for using in next stage

2) Storage Stage

After the compounding stage had been completed, the compounding samples were stored by placing in air at room temperature (30-35°C). Observation concerning storage time range from minute up to many hours were investigated. The foaming and cross-linking of the sample were analysed by using gas measurement apparatus and rheometer (detail in 3.4).

Table 3.5 Variation time in storage stage

Formulation No.	Compounding time			Storage time
	Stage 1	Stage 2	Stage 3	
No. 1-No. 7	*	*	*	15 min-18 hr

* Optimum condition from 1)

3) Cure Time/Temperature in The Cross-Linking/Foaming Process.

The compression molding using the condition obtaining from the previous result (optimum condition from 1),2)) was used for cross-linking/foaming of the sample from 2). The finished samples were analysed the physical properties (density, hardness, tensile strength, tear strength, compression set, expansion ratio, elongation and cell shape) using methods as described in 3.4.

Table 3.6 Variation cure time/temperature in cross-linking/foaming process

Formulation No.	Compounding time			Storage time	Corss-linking/foaming	
	Stage1	Stage2	Stage3		165°C	185°C
No.1-No7	*	*	*	*		

* Optimum condition from 1),2)

3.3.4 Replacement of Synthetic Polyisoprene by Natural Rubber in EVA Foaming Process

The result of observation in 3.3.3 were used as the basic idea for cross-linking/foaming of EVA blends (Formulation No.8-No.13). Only the important parameters were again observed.

Table 3.7 Variation process in cross-linking/foaming of EVA blends

Formulation No.	Investigation Step	Compounding time			Storage time	Cross-linking/foaming
		Stage1	Stage2	Stage3		
No.8-No.13	1)					
	2)					
	3)					

3.4 Determination of Physical Properties of EVA Foam

All EVA compound samples were analysed using the following methods :

- 1) Density : ASTM D-3575 Method A
- 2) Hardness : ASTM D-1415-88
- 3) Tensile strength : ASTM D-3575 or
ASTM D-412
- 4) Elongation : ASTM D-3575 or
ASTM D-412
- 5) Tear strength : ASTM D-3575 or
ASTM D-624
- 6) Compression Set : ASTM D-3575 Suffix B
- 7) Expansion ratio :

This ratio can be obtained by divided the foam volume of the sample which stored at room temperature for 24 hours with the mold volume:

For example :

$$\begin{aligned}
 &\text{-Foam volume (24 hours storage)} \\
 &= \text{Width} \times \text{length} \times \text{thickness} \\
 &= 156 \times 156 \times 14 \text{ mm}^3 \\
 &= 340,704 \text{ mm}^3 \\
 &\text{-Mold volume} \\
 &= 120 \times 120 \times 10 \text{ mm}^3 \\
 &= 144,000 \text{ mm}^3 \\
 &\text{-Expansion ratio} = \text{Foam volume/Mold volume} \\
 &= \frac{340,704}{144,000} \\
 &= 2.3
 \end{aligned}$$

8) Cell shape

Before cell shape observation , the sample preparation had to be done as followed:

1. By slide approximately 2 millimeter from the surface sample with a sliding machine (normal use in the shoe industry).

2. Slightly coat the surface sample with a blue ink to shade the cell figure for better observed and photoed by both microscope and camera.

The picture of cell shape was taken by camera through the microscope (with magnitude x 100 times).

9) Foaming

The sample (cut to small size, 3 gram) was place in the glass tube equiped with connecting silicone tube and the heating unit (temperature set at 165 or 185 °C) as shown detail of each equipments in Appendix D. The pressure of generated gas by the decomposition of blowing agent was measured by using a barometer which connect directly to the gas tube. Plot of the difference height of mercury in the barometer (before and after decomposition step) versus generating time had been done and the foaming was determined using this relation.

10) Shear viscosity

Approximately 65 g. of small sample (size 4x4x1 mm³) was placed into the barrel of the processability tester (Appendix F). The processability tester will provide viscosity and shear stress data at test conditions of actual processing shear rates and temperature.

For example :

Temperature (assigned) = 120 °C

Shear Rate (assigned) = 100 sec⁻¹

Shear Stress (data obtain from the tester) = 154 Psi

Shear Viscosity = Shear Stress/Shear Rate

In SI Units :

Shear viscosity = Viscosity constant x (Shear Stress)
Shear Rate

viscosity constant* (for L/D = 16:1)

= 6.996x10⁻¹ Pa.in³.s/min.lb

Shear viscosity = 6.996x10⁻¹ x(154/100) Pa.S

= 1.077 Pa.S

* This constant is obtained form the mamual of the processability tester.

11) Cross-linking

Sample (spherical 5 centimeter, approximately 20-25 gram) was placed in the sample receiver of a Rheometer (Appendix E) using cure temperature at 165 or

185°C. The torque data will be automatically plotted versus time by the plotter of the Rheometer during the operation. The graph was used to analyse the cure time.



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