CHARPTER III

EXPERIMENTALS

3.1 Materials

3.1.1 Shoe sole scrap

Shoe sole scrap is virtually alternated layers of composed of natural rubber (NR), ethylene-vinylacetate copolymer (EVA), and low density polyethylene (LDPE) as shown in Figure 3.1.

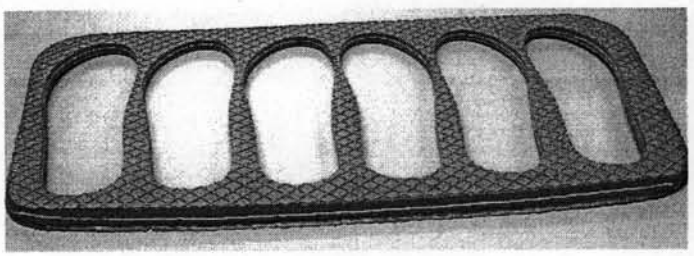

Fig. 3.1 Shoe sole scrap

3.1.2 Low density polyethylene (LDPE)

LDPE, LD1902F/FA, was provided by Cementhai co.Ltd., Thailand, in the form of homopolymer pellets with a density of 0.919 g/cm^3 and a melt flow index(MFI) of 2.0 g/10min.

3.1.3 Carbon black

Carbon black was supplied by JJ-Degussa chemicals (T) Ltd,. Under the trade name of Printex XE 2B.

3.1.4 Tetramethyl thiuram disulfide (TMTD)

Tetramethyl thiuram disulfide (TMT) was purchased Fluka, from A.C.S, Thailand

3.2 Instruments

3.2.1 Processing instruments

3.2.1.1 Microwave oven

Microwave oven (LG MS-2643C 28 Lt., 900 watt and 10 levels) was used to devulcanize shoe sole scrap (Fig. 3.2).

Fig. 3.2 Microwave oven (LG MS-2643C)

3.2.1.2 Ball mill

The precoating of the shoe sole scrap with carbon black was performed on a ball mill presented in Figure 3.3.

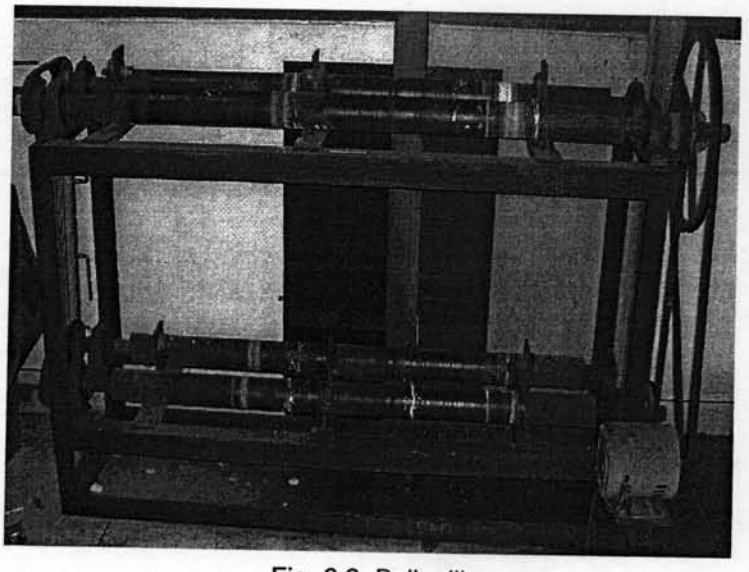

Fig. 3.3 Ball mill

3.2.1.3 Two-roll mills

The grinding and mixing of the components of the thermoplastic elastomers was carried out in the two-roll mill by a LABTECH engineering company.LTD, model LRM-S-200) (Fig.3.4).

Fig. 3.4 Two-roll mill (LABTECH model LRM-S-200)

3.2.1.4 Twin-screw extruder

After premixing, the blends were compounded, extruded, and pelletized by a Thermo PRISM co-rotating twin screw extruder model TSE-16-TC (Figure 3.5).

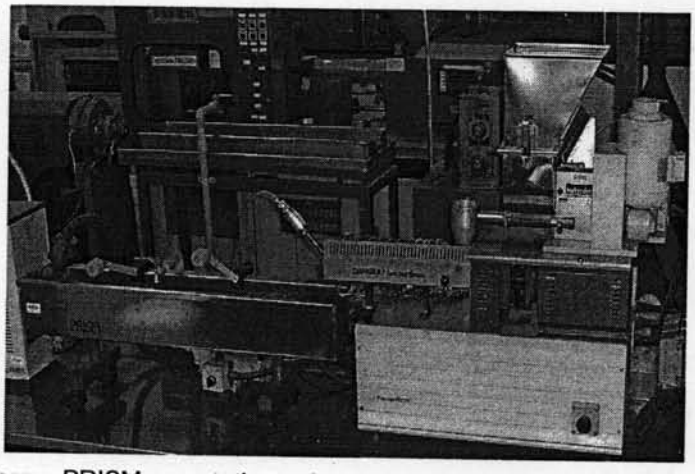

Fig. 3.5 Thermo PRISM co-rotating twin screw extruder model TSE-16-TC

3.2.1.5 Compression molding machine

The compounded pellets were pressed by a LABTECH compression molding, model LP-S-50 (Figure. 3.6).

Fig. 3.6 Compression molding machine(LABTECH model LP-S-50)

3.2.2 Characterizing and Testing instruments

The instruments used to characterize and test the prepared TPEs are listed in Table 3.1

Table 3.1 Characterizing and testing instruments

Characterizing and Testing	Instruments
Tensile properties	Universal Testing Machine (LLOYD LR 10KN)
Tear strength	Universal Testing Machine (Instron 446)
Hardness	Hardness tester (IRHD)
Abrasion resistance	Abrasion tester (Taber 5150)
Morphology	Scanning Electron Microscopy (JSM-4800 of JEOL Co.)
Viscoelastic properties	Dynamic Mechanical AnalyzerNETZSCH

3.3 Experiment of Procedure

The flow chart of the entire experimental procedure is shown below Figure 3.7.

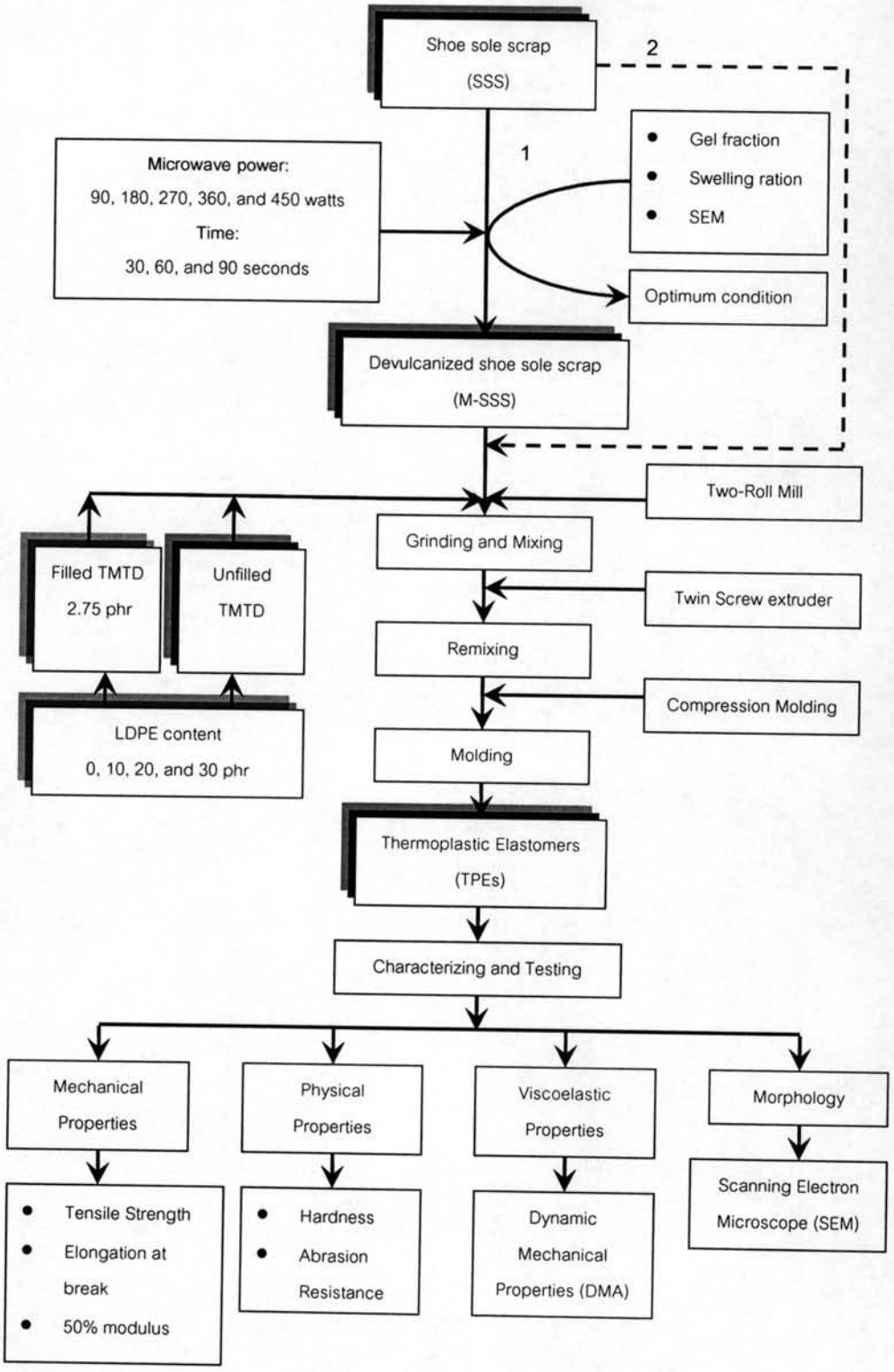

Fig. 3.7 Flow schematic diagram of the preparation and characterization of the thermoplastic elastomers (TPEs) from shoe sole scrap and low density polyethylene (LDPE).

3.3.1 Devulcanization of Shoe Sole Scrap

Shoe sole scrap (SSS) was devulcanized by microwave energy at various microwave power (i.e., 90, 180, 270, 360, and 450 watt) and time (i.e., 30, 60, and 90 sec). Prior to do so, the shoe sole scrap was precoated with carbon black (1 phr) to increase its heatability under microwave energy by mixing them in a ball mill for 6 hrs. The optimum condition for devulcanizing rubber was determined by using gel fraction, swelling ratio, and morphology of the devulcanized rubber.

3.3.2 Preparation of Thermoplastic Elastomers (TPEs)

The devulcanized shoe sole scrap was premixed with LDPE using a two-roll mill. First, the devulcanized SSS was ground in tight nip of a heated laboratory mixing mill at a friction ratio of 1:2 for 40 min at 60^{o}C. After 40 min of mastication, various ratios of LDPE was added to the ground or devulcanized SSS (which formed a powder meanwhile) and the mixing was continued for further 10 min. The ratios of shoe sole scrap/LDPE produced were 100:0, 90:10, 80:20, and 70:30. Additionally, 2.75 phr of tetra methyl thiuram disulfide (TMTD) was used as a reclaiming agent. Table 3.2 summarized the compositions of TPEs prepared in this work.

After premixing, the shoe sole scrap/LDPE were melt blended in a twin-screw extruder with L/D ratio = 30 and D = 2.5 cm. The extrusion was conducted at a speed of 25-30 rpm at a barrel temperature of 170, 175, 185^{o}C from feed zone to die zone, respectively. The extruded strands were then air-dried and pelletized.

Finally, the compounded pellets were compression molded into sheets by using a compression molding at a molding temperature of 180^{o}C and a pressure of 100 MPa. Thermoplastic elastomers sheets with dimension of 150 × 150 × 2 mm^{3} were obtained and used for subsequentmechanical and physical testing.

Table 3.2 Formulations of shoe sole scrap thermoplastic elastomers

Microwave energy	Reclaiming agent	SSS	LDPE
Without microwave energy	No TMTD	100	0
		90	10
		80	20
		70	30
	With TMTD (2.75 phr)	100	0
		90	10
		80	20
		70	30
Under optimized condition of microwave energy	No TMTD	100	0
		90	10
		80	20
		70	30
	With TMTD (2.75 phr)	100	0
		90	10
		80	20
		70	30

*Note that SSS is shoe sole scrap, LDPE is low-density polyethylene, and phr is part per hundred of resin.

3.4 Characterization and testing

3.4.1 Characterization of devulcanized shoe sole scrap

3.4.1.1 Determination of gel fraction and swelling ratio

The gel fraction and swelling ratio are direct measurement of the degree of crosslinking. The gel fraction and swelling ratio was determined with about 0.7 g of shoe sole scrap. The sample was immersed in pure toluene at room temperature for 48 h to allow the swelling to reach diffusion equilibrium. At the end of period, the test piece was taken out and

the adhered liquid was rapidly removed by blotting with blotting paper. Afterwards the swollen weight (w_2) was immediately measured. The sample was dried in a vacuum to obtain constant weight (w_1)and the desorbed weight was taken. The gel fraction and swelling ratio are defined as:

$$\% \text{ Gel fraction} = \frac{W_1}{W_0} \times 100 \quad \text{.....(3.1)}$$

$$\text{Swelling ratio} = \frac{W_2 - W_0}{W_0} \quad \text{.....(3.2)}$$

Where W_0 is the weight of the test piece before swelling , W_1 is the weight of the dried test spiece, and W_2 is the weight of the swollen test piece after immersed.

3.4.1.2 Morphology of devulcanized shoe sole scrap

The morphology of shoe sole scrap before and after microwave devulcanized was analyzed by the scanning electron microscope (SEM) (JEOL JSM-4800) at 15 KV.after coating the sample with gold to prevent surface charging under electron beam..

3.4.2 Characterization of thermoplastic elastomers (TPEs)

3.4.2.1 Mechanical properties

The tensile properties of TPEs were measured using a universal testing machine LLOYD LR 100K, according to the ISO 37 standard. The test was performed on dumbbell specimens at ambient temperature with on initial grip separation or gague length of 65 mm. The crosshead speed for the tensile test was set at 500 mm/min and 1 KN of load cell was used. All tests were performed at room temperature ($23 \pm 2^{\circ}C$). At least five specimens from each sample were tested.

Tear strength was determined by using Instron 446 with the crosshead speed of 500 mm/min according to the ISO 34 standard. Five angle specimens per sample were mearsured and averaged.

3.4.2.2 Physical properties

3.4.2.2.1 Hardness

Hardness is a property of considerable importance, usually included in rubber specifications along with the tensile properties. It may be defined as the resistance to indentation under conditions that do not puncture the rubber. The hardness reading depend on the dimension of the test piece, thickness being the most critical dimension. The initial reading of a Durometer depends on the duration of loading, both because of creep in the rubber. Since different materials have different creep characteristics, it is very important to precise that the rate of loading is standardized and the duration of loading is specified

The hardness measurements were performed according to the ISO 48 standard by The International Rubber Hardness Degrees (IRHD). The sample with a thickness of 2 mm was measured. At least five measurements for one piece of specimen were taken and the median of the results was taken, i.e. the middle value when these are arranged in increasing order .

3.4.2.2.2 Abrasion resistance

Abrasion resistance was determined by using Taber model 5150 according to ASTM D4060. TPEs were cut into a circular shape with 100 mm in its diameter and a thickness of 2 mm. Load and number of cycles used were 500 g and 1,000 cycle, respectively. The diagrammatic arrangement of Taber abraser test is shown in Fig. 3.8.

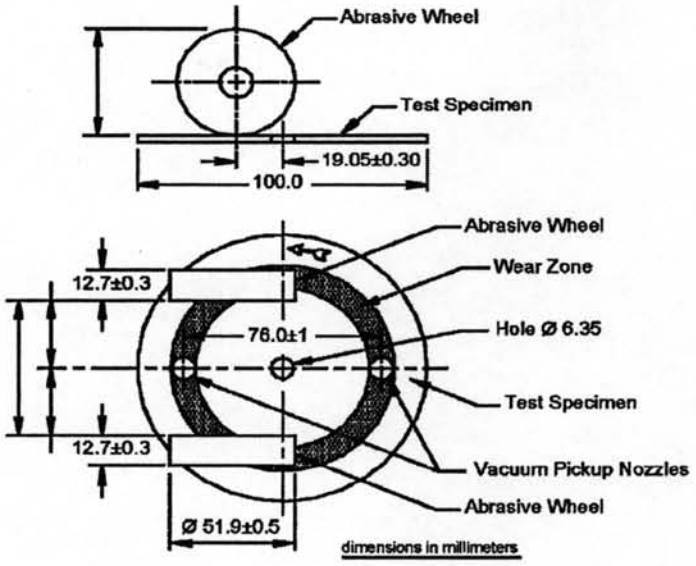

Fig. 3.8 Diagramatic arrangement of Taber Abraser Test.

3.4.2.3 Dynamic mechanical analysis (DMA)

The viscoelastic behavior of the resulting thermoplastic elastomers were investigated using a DMA (NETZSCH) in dual cantilever mode at frequency of 1 Hz. Compression-molded samples with the dimensions of 5 × 10 × 2 mm were used for testing. The samples were tested under nitrogen atmosphere at a temperature range of -80°C to 80°C and a heating rate of 3°C/min.

3.4.2.4 SEM studies of fractured surface

Morphology is a major determinant of the properties of heterogeneous polymer blends. For example, a large particle size and weak adhesion would result in poor mechanical properties in the blends. The main physical factors that determine the final morphology of the blends are component ratio, their intrinsic melt viscosity, rate of shear during melt mixing, and the presence of other ingredients.

The morphology of tensile fractured surface of the shoe sole scrap/LDPE composites was characterized by a scanning electron microscope (SEM) (JEOL JSM-4800) at 15 KV. The fractured surface was sputter-coated with a thin layer of gold at a zero degree felt angle before being scanned to avoid surface changing under electron beam.