

CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 Materials

3.1.1 Poly(vinyl chloride), PVC

There are two types of PVCs used for this study like rigid PVC (unplasticized PVC, R-PVC) and soft PVC (plasticized PVC, S-PVC). Both of them are the same K value (K 66) and supplied from Thai Plastic and Chemical company (TPC).

3.1.2 Tire-Rubber Wastes

There two types of tire-rubber wastes, ground rubber tire (GRT), UCD-103 as its trade name, and reclaimed rubber tire (RTR), which most of the metal and polyester cord had been separated. Both components are from Union Commercial Development.

3.1.3 Chlorinating Agent

Trichloroisocyanuric acid (TCICA) is used as a chlorinating agent for surface modification of tire rubber. This compound is supplied from KC salt company.

3.1.4 Compatibilizers

There are two compatibilizers used for this study; chlorosulfonated polyethylene (CSPE or Hypalon 40) from Polymer Innovation CO.,LTD., and nitrile butadiene rubber (NBR or Nipol DN3350) from Zeon Corporation CO.,LTD.

3.2 Instruments

Instruments and machine used in this study are listed in **Table 3.1**

Table 3.1 List of instruments used for this research.

NO	Instrument	Model	Purpose/Information
1	Two roll mill	Lab Tech/Lab Tech.	Mixing of polymers
2	Compression Mold	Lab Tech/Lab Tech.	Molding the mixed polymers
3	Universal Testing Machine	LR 5K/LLOYD instrument	Tensile strength and % Elongation
4	Impact tester	GT7045/GOTECH	Impact Strength
5	Durometer	Teclock/Type D	Hardness
6	Differential Scanning Calorimeter(DSC)	DSC7/PERKIN ELMER	Compatibility
7	Dynamic Mechanical Thermal Analyzer (DMTA)	DMTA4/Rheometric Scientific.	Compatibility
8	Scanning Electron Microscope (SEM)	JSM-5800/JEOL	Morphology and Compatibility
9	X-ray Fluorometer (XRF)	PW2400/Philip	Chloride content
10	Thermalgravimetric Analyzer (TGA)	TGA7/PERKIN ELMER	Composition of tire rubber wastes

3.3 Experimental Procedure

3.3.1 Acetone extraction

Commercial grade acetone (500ml), was added in 1 L round bottom flask. Then equip flask with soxhlet extractor containing 500 g the recycled tire-rubber 500 g. The recycled rubber was extracted for 24 hours. Then the extracted rubber was removed and dried in the oven for 24 hours at 50°C.

3.3.2 Tire-rubber waste compositions.

The determination of the main composition of reclaimed tire rubber (RTR) and ground rubber tire (GRT) was performed by means of thermogravimetric Analyzer (TGA). Ten mg of tire rubber waste sample was heated from 50°C to 550°C (10°C/min , N₂ atmosphere) and 550°C to 850°C (10°C/min , O₂ atmosphere). The sample compositions such as the percentage of polymer, carbon black, and residue were reported.

3.3.3 Chlorination of tire rubber wastes.

The used tire rubber particles were acetone extracted and then dried at 50°C for 24 hours in the oven. Next the particles were immersed in a freshly prepared TCICA solution in methanol for 20 min. The particles were then filtered, washed thoroughly with water and dried for 24 hours at 50°C. The chlorinated tire rubber wastes, GRT and RTR treated with TCICA solution, were designated as Cl-GRT and Cl-RTR, respectively. Since the amount of chlorine deposited on the rubber surface having to be analyzed by means of X-ray photoelectron spectrometer (XPS or ESCA), the chlorine content could not be directly determined because this XPS was not available in Thailand. Both XRF and DMTA were used instead.

3.3.4 Formulations

Formulation and composition of PVC blend.

PVC was firstly melted in a two-roll mill which the temperature of the front and back roll were set at 170°C and 175°C respectively for 5 min. Then the tire-rubber wastes such as GRT, RTR, Cl-GRT or Cl-RTR was added to the melt PVC that the recipe of mixing was followed as **Table 3.2**. The molten polymer were cut diagonally from time to time and folded over several times during mixing. After 10 minutes of mixing, the well-mixing samples were sheeted out at a 2 mm nip gap on a two-roll mill. The sheet out compounds were compression molded in an electrically heated hydraulic press at 180°C for 2 min at 150 kg/cm² pressure and then cooled under pressure by water circulation through the hot platens of dimension 18X12 cm.

For finding the optimum chloride content on the modified surface of tire rubber wastes by using TCICA solution in methanol, the modified RTR and modified GRT were added to R-PVC. Their recipes are shown in **Table 3.3**.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.2 Formulation of PVC/GRT, PVC/RTR, PVC/CI-RTR and PVC/CI-GRT

PVC	No	RTR (phr)		GRT (phr)		Compatibilizer	
		Unmodified	Modified	Unmodified	Modified	CSPE	NBR
Plasticized	I1	10	-	-	-	-	-
	I2	20	-	-	-	-	-
	I3	30	-	-	-	-	-
	J1	-	-	10	-	-	-
	J2	-	-	20	-	-	-
	J3	-	-	30	-	-	-
	J4	-	-	40	-	-	-
	Unplasticized	E1	10	-	-	-	-
E2		20	-	-	-	-	-
E3		30	-	-	-	-	-
E4		40	-	-	-	-	-
E5		-	10	-	-	-	-
E6		-	20	-	-	-	-
E7		-	30	-	-	-	-
E8		-	40	-	-	-	-
E9		-	50	-	-	-	-
F1		-	-	10	-	-	-
F2		-	-	20	-	-	-
F3		-	-	30	-	-	-
F4		-	-	40	-	-	-
F5		-	-	50	-	-	-
F6		-	-	-	10	-	-
F7		-	-	-	20	-	-
F8		-	-	-	30	-	-
F9		-	-	-	40	-	-
F10		-	-	-	50	-	-
F11		-	-	-	60	-	-
G1		-	40	-	-	-	-
G2		-	40	-	-	10	-
G3		-	40	-	-	20	-
G4		-	40	-	-	30	-
G5		-	40	-	-	-	10
G6		-	40	-	-	-	20
G7		-	40	-	-	-	30
H1		-	-	-	-	50	-
H2		-	-	-	-	50	10
H3		-	-	-	-	50	20
H4		-	-	-	-	50	30
H5		-	-	-	-	50	-
H6		-	-	-	-	50	-
H7		-	-	-	-	50	-

Table 3.3 Formulation of PVC compounds contained 30 and 40 part of RTR and GRT per 100 part of R-PVC

Rubber	No	% TCICA solution in methanol			
		0	1	3	5
RTR	R0	30	-	-	-
	R1	-	30	-	-
	R3	-	-	30	-
	R5	-	-	-	30
GRT	G0	40	-	-	-
	G1	-	40	-	-
	G3	-	-	40	-
	G5	-	-	-	40

3.3.5 Measurement of physical properties.

Tensile properties measurement

Dumbbell-shapes tensile specimens were punched out from the mold sheets. Tensile strength and % elongation were measured, according to ASTM D412-98a specification, in a Zwick Universal testing machine (UTM) model LR 5K LLOYD at a strain rate of 500 mm/min at 25°C

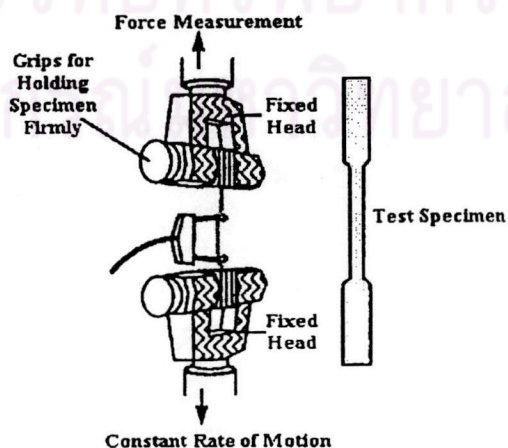


Figure 3.1 Tensile testing apparatus and test specimen.

Izod impact strength testing

Izod impact strength specimens were prepared by following ASTM D256-81. A pendulum swung on its track and struck a notched, cantilevered plastic sample. The energy lost, required to break the sample, as the pendulum continued on its path was measured from the distance of its follow through. For hardness of 3 mm-thick, it was measured by using Durometer type D.

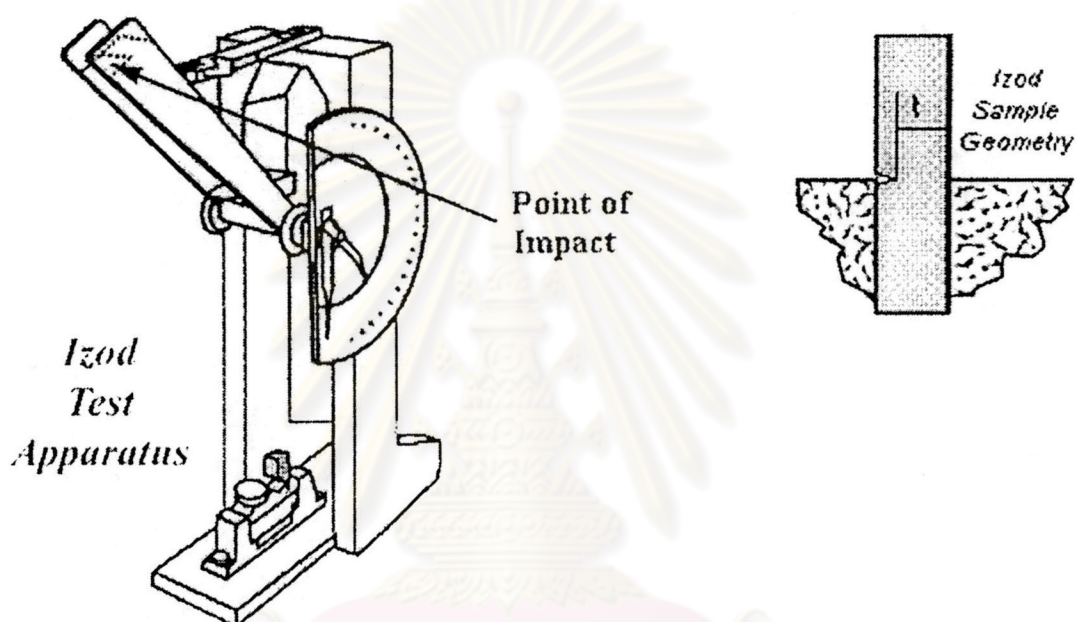


Figure 3.2 Izod impact strength apparatus and test specimen.

3.3.6 Measurement of thermal properties

Differential Scanning Calorimetric (DSC) study

The glass-transition temperature of all composited samples and raw materials was investigated by DSC. 8 mg of sample was heated from -150°C to 120°C with scanning rate of $10^{\circ}\text{C}/\text{min}$, which confirmed the miscibility of each sample.

Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical data of the blends were obtained using a dynamic mechanism thermal analyzer (DMTA) DMTA4/Rheometric Scientific. Sample specimens of dimension 45X8X3 mm. were analyzed in dual cantilever bending mode at a constant frequency of 1 Hz, peak to peak displacement of 64 μm , and in the temperature range from -100°C to 50°C . The heating rate was $3^{\circ}\text{C}/\text{min}$. The temperature corresponding to the peak in $\tan \delta$ vs temperature plot was taken as the glass-to-rubber transition temperature (T_g).

3.3.7 Morphology

Morphology of the molded compositions was examined under the scanning electron microscope (JEOL JSM 5800) by fracturing the specimens in liquid nitrogen and then etching out the rubber part like GRT, RTR, CI-GRT or CI-RTR in boiling concentrated nitric acid (115°C) for 10 min. The samples were washed with water and dried at room temperature. Etched out samples were gold coated and then examined under the SEM.

3.3.8 Swell Behaviors

Square test pieces of dimension 10X8X3 mm were die-cut from the molded sheet of used rubbers; GRT, RTR, CI-GRT or CI-RTR. All specimens were swollen in toluene at 30°C for 96 hours. The swollen samples were put on a slide and covered with a light cover slip. Under this condition, sample weights were measured. The average value of five such measurements was noted. The percent swelling weight was obtained from the following equation:

$$\text{Percent swelling} = \left(\frac{W_2 - W_1}{W_1} \right) \times 100$$

Where W_1 and W_2 are the average weights of unswollen and swollen one, respectively.