CHAPTER IV
EXPERIMENT

In the present study, effects of molecular weight and weight ratio of syndiotactic polystyrene on mechanical properties were investigated. Moreover, the polymer blend between polystyrene and the selected polymer was examined. The details of the experiments were explained as in the following. In this chapter, the materials and chemicals, equipments, characterization instruments and sample preparations will be explained.

4.1 Materials and Chemicals

4.1.1 Chemicals

1. Two molecular weight of Syndiotactic Polystyrene (sPS) commercial grade without additives was supported by Idemitsu Kosan Co. Ltd.

   sPS1= sPS Mw. 31.7 x 10^4

   sPS2= sPS Mw. 13.0 x 10^4

2. Poly (alpha methylstyrene), (PaMS) was purchased from Scientific Polymer Products, Inc.

3. Poly (n-butyl methacrylate), (PBMA) was purchased from Scientific Polymer Products, Inc.

4. Poly (cis-isoprene), (PIP) was purchased from Scientific Polymer Products, Inc.

5. Poly (ethyl methacrylate), (PEMA) was purchased from Scientific Polymer Products, Inc.

6. Poly (cyclohexyl methacrylate), (PHMA) was purchased from Scientific Polymer Products, Inc

7. Nitrogen gas (Ultra high purity grade, 99.999 %) was purchased from Thai Industrial Gas Co.,Ltd.(TIG).

4.1.2 Materials

1. Aluminium moulds 100x100x0.5 mm. with drilled 10x50x0.5 mm were purchased from P. Konlakan Machienery Tool.

2. 2 Steel plates 150x150x2 mm. were purchased from P. Konlakan Machienery Tool.

3. Blending spoons were purchased from Lotus Supermarket.

4.2 Equipments

4.2.1 Digital Hot Plate Stirrer

The Cole-Palmer which is a programmable digital laboratory hot plate was used for preparing samples by melted mixing between Syndiotactic Polystyrene and selected polymer. All functions can be set from digital panel and display their status on LCD. The plate temperature, stir speed and time are controllable.

4.2.2 Automatic Hydraulic Hot Press

The LAB TECH hydraulic hotpress LP-50 M/C 9701 was used for preparing the thin film form polymer blend between Polystyrene and selected polymer. It has both the automatic mode and manual mode. In automatic mode, it has four steps (preheat, vent, full press and cooling step), that can be controlled in one touch which times adjustment of each of step separately. The hot press can be compressed up to maximum 50 ton (160 kg/cm^2).

4.3 Analysis Instruments

4.3.1 Differential Scanning Calorimetry (DSC)

The melting and glass transition temperature of the polymers were determined with a Perkin-Elmer DSC-Pyris Diamond. The analyses were performed at the heating rate of 40°C/min. The heating cycle was run twice. In the first scan, samples were heated up and then cooled down to initial temperature. In the second scan, samples were reheated at the same rate. Both the results of the first and second scan were reported.
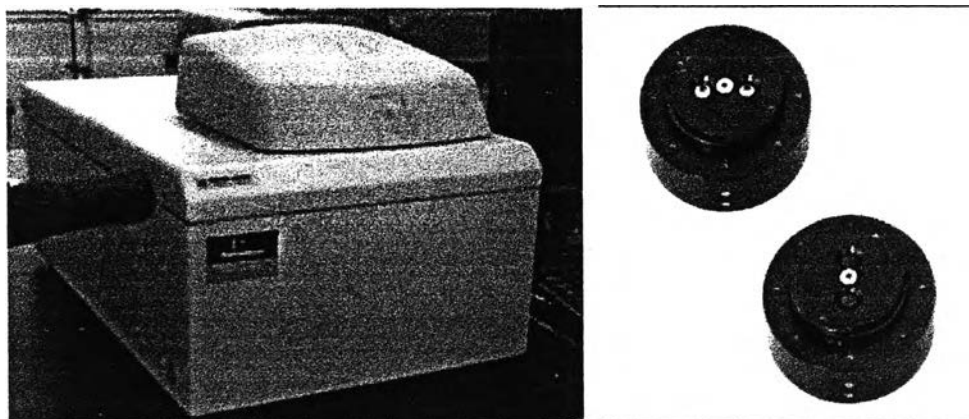
Figure 4.3.1 Differential Scanning Calorimetry (DSC) Equipment

4.3.2 Thermal Gravity Analyzer (TGA)

Decomposition of polymer normally uses thermal analysis. Thermal gravimetric analyses (TGA) of the samples were performed on a thermal analyzer (Perkin-Elmer TG/DTA-Pyris Diamond). The sample was cut to pieces with 2 mm length and 2 mm width, and then analyzed under nitrogen atmosphere with a flow capacity of 100 ml/min at a heating rate of 20 °C/min from 50 to 400 °C.
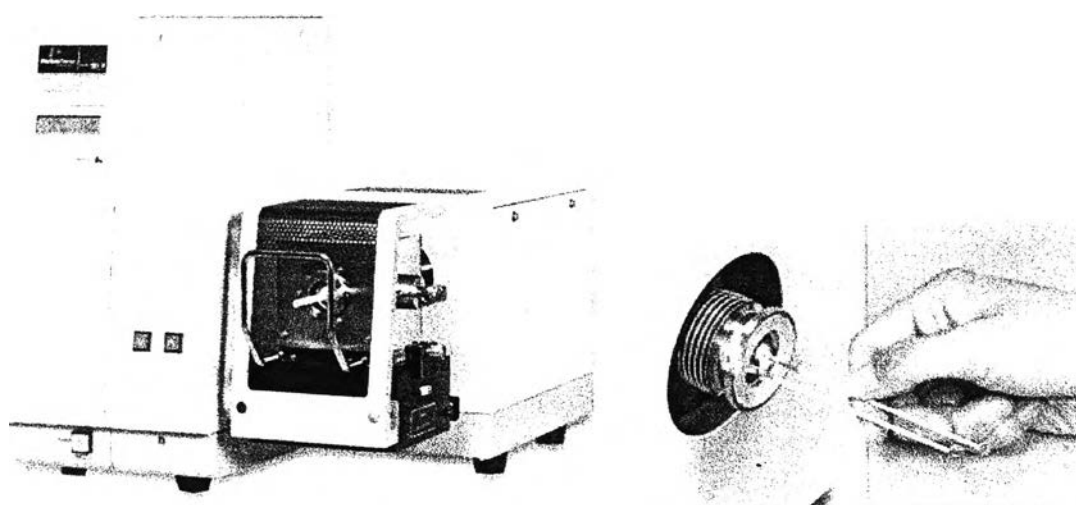

Figure 4.3.2 Thermal Gravity Analyzer (TGA) Equipment

4.3.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was performed to determine E' curve as the function of frequency and time at constant temperature using Perkin-Elmer DMA-Pyris Diamond. The film was analyzed under nitrogen atmosphere with isothermal technique. It was operated by using step change of temperature every 20 C.
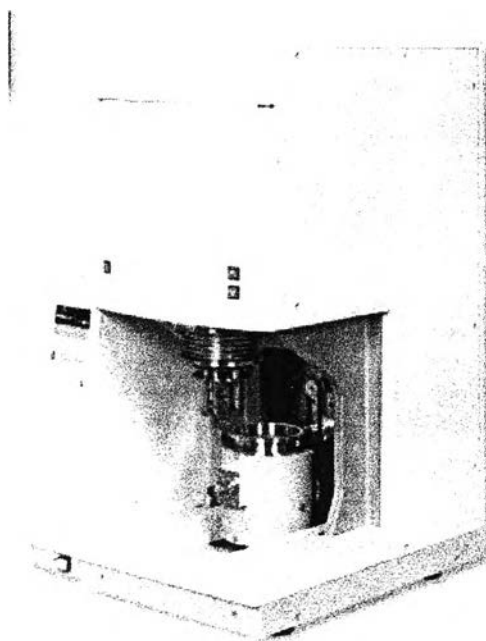

Figure 4.3.3 Dynamic Mechanical Analysis (DMA) Equipment

4.4 Procedures

4.4.1 Preparation

4.4.1.1 Samples Preparation

Both molecular weights of Sydiotactic Polystyrene (sPS), Poly(cyclohexyl methacrylate) (PHMA), Poly(ethyl methacrylate) (PEMA), Poly(n-butyl methacrylate) (PBMA) and Poly(cis-isoprene) (PIP) were weighted. For purpose of this thesis, sPS was chosen for main component and compared with previous work. The ratio by weight of sPS and other polymers will be 80:20.

4.4.1.2 Blend Preparation

The blends were made by melt mixing at 300°C by hand on the digital controllable hot plate with various type of polymer.

4.4.1.3 Molding Preparation

After blending, all polymer blends was molded with Automatic Hydraulic Hot Press. Hot Press was opened to warm at 300 °C before using about half hours. Then steel plate that coated with aluminium foil, aluminium mould and blend polymer were putted down to Hot Press respectively. When the polymer blend was melt, other steel plate that coated with aluminium foil was putted down to melt blend polymer. Next they will be slowly compressed until 1500 psi. The blend polymer was annealed at 300 °C by kept in Hot Press about 5 minutes and immediately quenched to 200°C for twenty minutes before further experiments at room temperature. The size of blend polymer after molding was 10x50x0.5 mm.

4.4.2 Polymer blend Characterization

4.4.2.1 Differential Scanning Calorimetry (DSC)

The melting temperature and glass transition temperature of the polymers were determined with a Perkin-Elmer DSC-Pyris Diamond. The amount of samples was about 10-20 mg. The analyses were performed at the heating rate of 40°C/min. The heating cycle was run twice. In the first scan, samples were heated up and then cooled down to initial temperature. In the second scan, samples were reheated at the same rate. The temperature ranges for first and second scan were shown in Table 4.1. Both the results of the first and second scan were reported

Table 4.1 Temperature range for DSC measurement

System	Temperature Heat up 1(°C)		Temperature Heat up 2(°C)	
	initial	final	initial	final
sPS	45	300	45	300
sPS/PIP	-50	300	-50	300
sPS/PBMA	20	300	20	300
sPS/PEMA	15	300	15	300
sPS/PHMA	-10	300	-10	300
sPS/PaMS	60	300	60	300

4.4.2.2 Thermal Gravity Analyzer (TGA)

Thermal gravimetric analyses (TGA) of the samples were performed on a thermal analyzer (Perkin-Elmer TG/DTA-Pyris Diamond). The sample was cut to pieces with 2 mm length and 2 mm width, and then analyzed under nitrogen atmosphere with a flow capacity of 100 ml/min at a heating rate of 20 °C/min from 50 to 400 °C. Relationships between sample temperature and loss weight were reported.

4.4.2.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of blending polymers were determined by using Dynamic Mechanical Analysis (DMA) with a Perkin-Elmer DMA-Pyris Diamond. The samples after molding were cut for standard DMA samples (10x25x0.25 mm). Condition and parameters were shown in Table below.

Table 4.2 Conditions and parameter for running DMA

Conditions and parameter	Value
Sample size(w x l x t) (mm)	10 x 25x0.5
DMS Measurement Mode	Tension
Temperature Control Mode	Ramp
DMS frequency (Hz)	0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0 50.0, 100.0
L Amplitude (μm)	10
Minimum Tension/Compression Force(mN)	200
Tension/Compression Force gain	1.5
Force Amplitude Default Value (mN)	4000
Nitrogen as carrier gas (ml/min)	100

For temperature program setting, the temperature was set at any temperature with isothermal running. The temperature was varied over and below those glass transition temperatures (T_g) of blending polymer.

4.4.3 Applying Data

The data from polymer blend characterization was modified to use in discussion part.

4.4.3.1 Differential Scanning Calorimetry (DSC)

From DSC information, glass transition temperature of polymer blends was compared with previous work. It was considered as miscibility and decreasing of glass transition temperature.

4.4.3.2 Thermal Gravity Analyzer (TGA)

From TGA information, amount of loss weight of polymer blends was calculated as 5 % and 10% percentage of loss weight. Temperature at those loss weights was compared for every blend system.

4.4.2.3 Dynamic Mechanical Analysis (DMA)

E' versus time and frequency at any temperature from DMA information was modified to create master curve and finding WLF constants. The step shown in below (shown as time dependence only);

Step1: Plot E' versus time at any temperature in the same log-log graph.

Step2: Choose reference temperature. In this work, the reference temperature was their glass transition temperature (T_g)of polymer blend.

Step3: Horizontally Shift curve to T_g curve by multiply factor value to them until curves intersect. Then, another curves was shift to previous curve by different factor value. After shift every curves, the master curve was exactly created. The example show in Figure below.
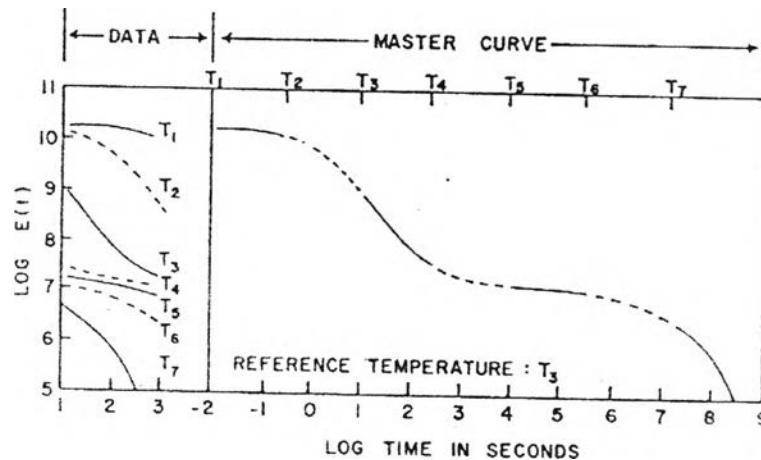

Figure 4.4.1 Example for preparation of a Stress Relaxation Master Curve from Measured Modulus-Time Curves at Various Temperatures

Let us now consider that these corrections have been made to the experimental curves on the left hand side of Figure. The curve at T_3 is reproduced on the right hand side of the figure. Next, the curve at T_2 is shifted to the left giving rise to the dotted extension of the $E(T_3,t)$ curve. This process is repeated until the complete master curve is formed. The a_T's are functions of temperature and are known as the shift factors. In our example, all of the curves at temperature higher than T_3 are shifted to

the right, those at T_1 and T_2 are shifted to the left. It should be clear that any temperature might have been chosen as the reference temperature. If T_4 had been chosen, for example, some of the shift factors would have been larger than 1.0 -those at lower temperatures-while some of the shift factors would have been less than 1.0-those at temperatures higher than T_4.

Step 4: Find WLF constants by develop WLF equation to fix curve

From WLF equation

$$\log a_T = \frac{-c_1(T-T_g)}{c_2+T-T_g}$$
4.4.1

Rearrange

$$\frac{-1}{\log a_T} = \frac{c_2}{c_1}\frac{1}{(T-T_g)} + \frac{1}{c_1}$$
4.4.2

From equation above, plot $-1/\log a_T$ versus $1/(T-T_g)$ then straight line was created so slope is c_2/c_1 and intercept-y axis is $1/c_1$. So c_1 and c_2 was determined.