

## CHAPTER II

### EXPERIMENTAL SECTION

#### 2.1 Materials

##### 2.1.1 Polymers

Poly(isoprene) (PI) and poly(styrene) (PS) were used as homopolymers, and poly(isoprene-1, 4-*b*-styrene) [P(I-*b*-S)] was used as a compatibilizer in this work.

The commercial grade poly(isoprene) (PI) was purchased from Japan Synthetic Rubber Co., Ltd. The laboratory grade poly(styrene) (PS) was purchased from Polyscience, Inc. The molecular weight of PS as given by the supplier is 50,000. The laboratory grade poly(isoprene-1, 4-*b*-styrene) [P(I-*b*-S)] was purchased from Polyscience, Inc. The molecular weight quoted on the diblock copolymer is 135,000 (67,500/67,500), and  $M_w/M_n = 1.06$ .

##### 2.1.2 Solvent

The analytical grade toluene, used as solvent for polymer solutions, was purchased from J. T. Baker.

## 2.2 Sample Preparations

The samples were prepared by solvent casting. The required thickness of the films was 0.4-0.5 mm.

### 2.2.1 Polymer Solution

Blends of the required composition were prepared by making solutions containing 8% by weight of total polymer in toluene. The polymer solution was stirred with 200 rounds/min at the room temperature for 48 hours, and then casted in the Petri dishes.

### 2.2.2 Polymer Films

The well-mixed polymer solution was casted in the Petri dish. the diameter of Petri dish is 5 cm. The Petri dish was covered with an aluminium foil before the polymer solution was casted, so that the polymer film would be removed easily with the aluminium foil. For the solvent evaporation, cares were taken about the dust, the humidity and the temperature. The solvent was evaporated at the room temperature for 5 days. Final solvent removal was done in a vacuum oven at 60°C for 48 hours (Akiyama and Jamieson, 1992). After the solvent had been eliminated from the casted films, the polymer films were allowed to settle at the room temperature 1-2 days for the sample relaxation. Then the polymer films were carefully removed from the Petri dish with the aluminium foil attached. For the pure PS film and the PS matrix film with a small amount of PI, the polymer films were carefully and slowly removed from the Petri dish because they were quite brittle. When the polymer film was removed from the

aluminium foil, we were careful to avoid any applied stress which might give a deformation to the polymer film.

The polymer films were sectioned from the center of the sample for homogeneity. They were sectioned into two different shapes, rectangular and dish. For extension analysis measurement, the dimensions of the film were 2.0 mm. in width (x), 2.0 mm. in height (y), and 0.4-0.5 mm. in depth (z). For parallel plate analysis measurement, the dimensions of the film were 8.0 mm. in diameter (d), and 0.4-0.5 mm. in height (y).

## 2.3 Sample Characterizations

### 2.3.1 Molecular Weight Determination

The molecular weight of PI was calculated by using the Mark-Houwink equation.

$$[\eta] = KM^a, \quad (2.1)$$

From this equation, the viscosity average molecular weight ( $\bar{M}_\eta$ ) can be calculated with known **K** and **a** values.

The constant values of **K** and **a** for a given polymer, solvent and temperature system were obtained from W. H. Beattie and C. Booth (1963).

In the W. H. Beattie and C. Booth work, the Mark-Houwink equation used for PI in toluene at 30°C has

$$\mathbf{K} = 2.00 \times 10^{-2} \text{ (ml/g)}, \quad \mathbf{a} = 0.728.$$

$\bar{M}_w$  of PI was measured and found to be  $1.024 \times 10^6$ .

### 2.3.2 Glass Transition Temperature Determination

Glass transition temperature ( $T_g$ ) of PI and PS were determined by the transition temperature of the maximum loss modulus peak for each component as measured by DMA.

$$T_g \text{ of PI} = -45.4^\circ\text{C},$$

$$T_g \text{ of PS} = 86.2^\circ\text{C}.$$

## 2.4 Dynamic Mechanical Analyzer

The DMA apparatus is the model 7-e from the Perkin-Elmer Corporation. The system has three separate units; they are computer (Digital), DMA 7-e (Dynamic Mechanical Analyzer), and TAC 7/DX (Thermal Analysis Instrument Controller) (figs. 2.1-2.2). With Perkin-Elmer 7 Series/UNIX Thermal Analysis System software installed in the workstation, the DMA 7-e was used for the quantitative and qualitative mechanical analysis of sample materials.

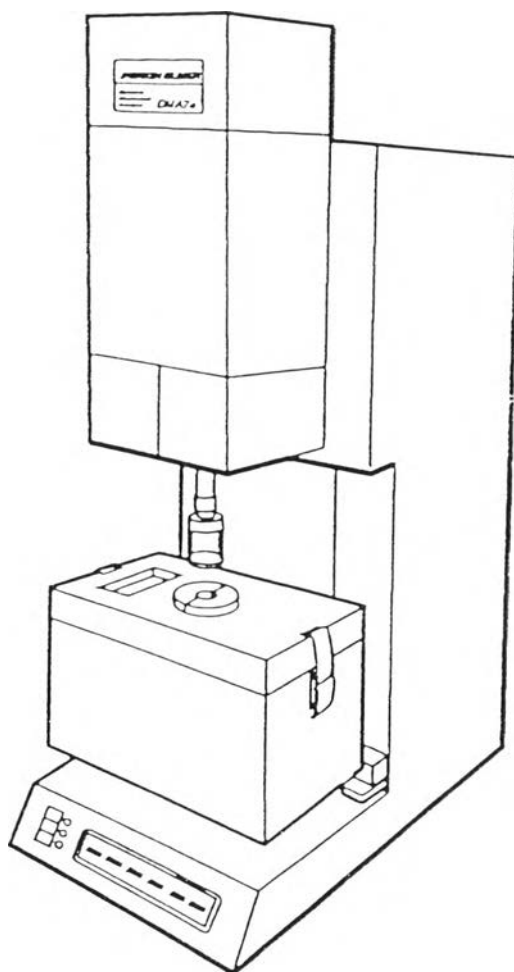
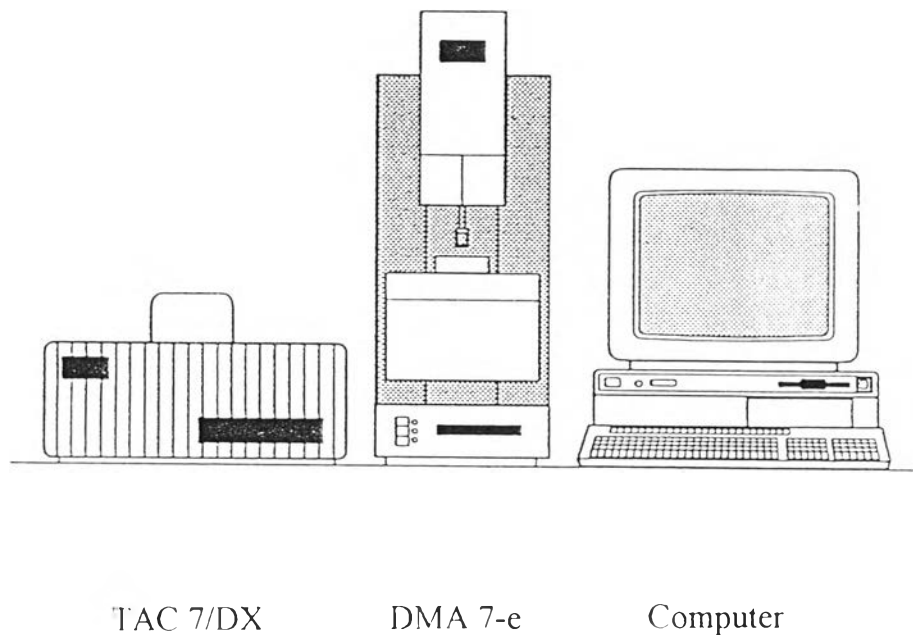


Figure 2.1 DMA 7-e Dynamic Mechanical Analyzer.



**Figure 2.2** DMA 7-e system.

#### **2.4.1 Principle of Dynamic Mechanical Analyzer**

Dynamic mechanical properties can be determined by measuring the response (deformation) of samples when they are subjected to periodic forces. Thus, amplitude, frequency, and type of oscillation are our experimental input parameters.

In the study of the response of a material to periodic forces, stress, strain, and frequency are the key variables. The stress applied to a viscoelastic body results in a linear or nonlinear dynamic response. For a linear response, if the stress varies sinusoidally with time at a given frequency,

the strain will vary cyclically at the same frequency. If the amplitude of the stress is small enough, the strain is also sinusoidal with time, and the amplitude of the strain is proportional to the amplitude of the stress at a given temperature and frequency; ie, the behavior is linear. However, if the amplitude of the stress is sufficiently large, the strain will vary at the same frequency but will be nonsinusoidal; it can have higher harmonics, showing nonlinear viscoelastic behavior.

The method of sinusoidal excitation and response is very useful for determination of the dynamic mechanical properties of polymeric materials. The applied force and the resulting deformation both vary sinusoidally with time; the rate is usually specified by the frequency  $f$  in Hz or  $\omega = 2\pi f$  in rad/s. For linear viscoelastic behavior, the strain alternates sinusoidally but is out of phase with the stress. This phase lag results from the time necessary for molecular rearrangements and is associated with relaxation phenomena. The stress  $\sigma$  and strain  $\varepsilon$  can be expressed as follows:

$$\varepsilon = \varepsilon_0 \exp i\omega t, \quad (2.2)$$

$$\sigma = \sigma_0 \exp i(\omega t + \delta), \quad (2.3)$$

Then,

$$\sigma/\varepsilon = K^* = (\sigma_0/\varepsilon_0) e^{i\delta}, \quad (2.4)$$

$$(\sigma_0/\varepsilon_0) e^{i\delta} = (\sigma_0/\varepsilon_0) (\cos \delta + i \sin \delta), \quad (2.5)$$

$$K^* = K' + iK''. \quad (2.6)$$

The real part of the compressive modulus  $K'$ , is called the storage modulus, because it is related to the storage of energy as potential energy and its release in the periodic deformation. The imaginary part of the

compressive modulus.  $K''$ , is called the loss modulus and is associated with the dissipation of energy as heat when the materials are deformed. In fig. 2.3, it is shown how the DMA works, in relation with the description given. In fig. 2.4, the definition of  $K'$  and  $K''$  as a viscoelastic ball is shown.

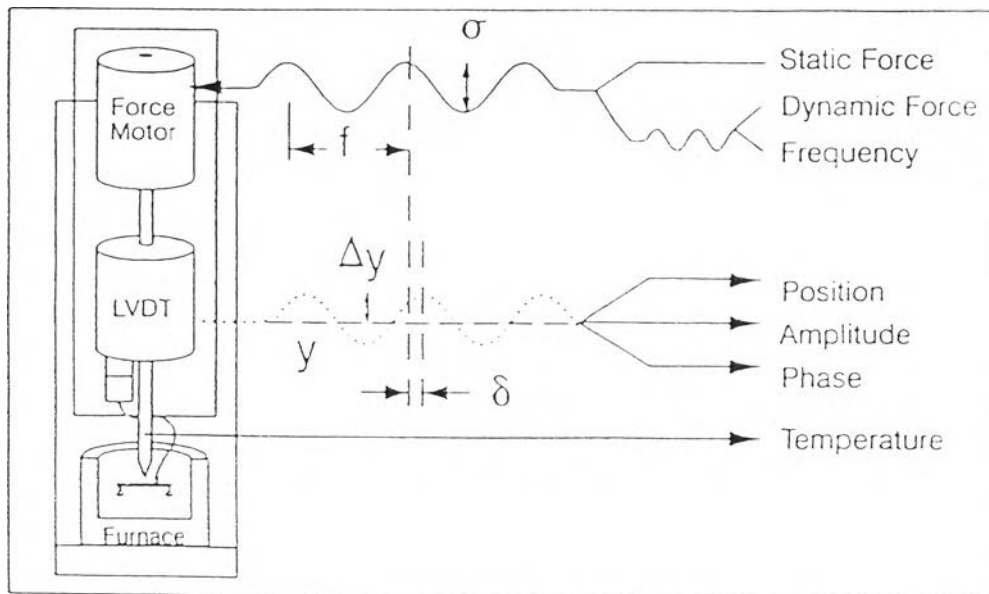


Figure 2.3 DMA 7-e Motor Control Variables.

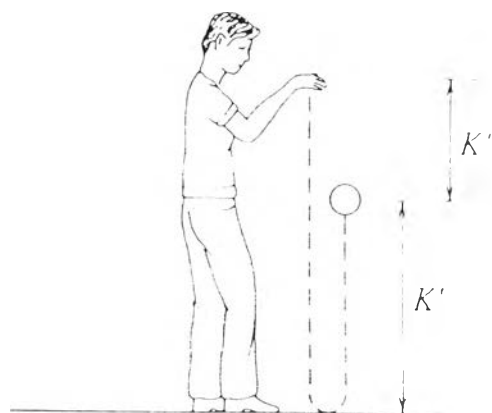


Figure 2.4 Simplified definition of  $K'$  and  $K''$

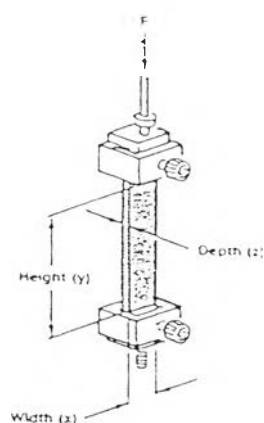


### 2.4.2 Measuring Systems

In this study, we used two measuring systems; the extensional analysis system which was used to study Young's modulus of the blends, and the parallel plate measuring system which was used to study the compressional dynamic moduli of the blends.

#### (a) *Extension*

The extensional analysis system was used to study low modulus materials such as thin films, textiles and other fibers, and hair. The Stainless Steel Extension Kit (Part No. N539-0132) has two clamping fixtures (fig. 2.5).



**Figure 2.5** Extensional Analysis Measuring System: Stainless Steel Parallel Clamp.

(b) *Parallel Plate*

The parallel plate measuring system was used to study materials ranging from those with honey-like consistency to thermoplastics and rubbers above their glass transition temperature. The Stainless Steel Parallel Plate Kit (Part No. N519-0133) has stainless steel parallel plates with diameter of 10 mm. (fig. 2.6).

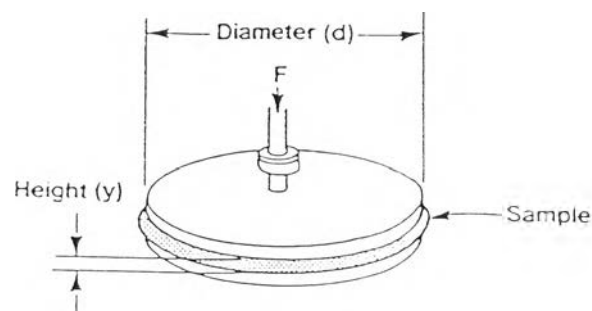


Figure 2.6 Parallel Plate Measuring System: Stainless Steel.

### 2.4.3 Operating Modes

The Dynamic Mechanical Analyzer can be operated in many different modes. A mode is defined as a software state where a selected variable (or variables) is programmed and all other variables are held constant.

(a) *Temperature Scan Mode*

In the Temperature Scan mode, the temperature is programmed and the frequency and stress are held constant. Temperature-dependent behavior is characterized by monitoring changes in strain and

phase. Alpha, Beta, and Gamma transitions may be identified as functions of temperature or time. Modulus and viscosity, as well as other standard rheological variables, may be readily obtained for these materials as functions of temperature or time.

*(b) Creep-Recovery Mode*

The temperature can be held constant or changed during a run, and there is no dynamic stress applied. In this mode, a constant stress rate is applied and held constant and the strain is monitored.

**2.4.4 Measurements**

There are two different measurements in this research: the dynamic mechanical measurement and the transient mechanical measurement.

*(a) Dynamic Mechanical Measurement*

The sample were measured by parallel plate probe in temperature/time scan mode. The measurement was taken from -150°C to +250°C with a rate of 5°C/min. Liquid nitrogen was used for cooling. Frequency of 5 Hz was used in this measurement. Heating rate was not higher than 5°C/min.

The effects of composition ratio and the effects of % block copolymer on the dynamic modulus (loss modulus and storage modulus) were studied in the dynamic mechanical measurement.

*(b) Mechanical Measurement*

The samples were measured by extension probe in the creep/recovery mode at the room temperature. Stress rates were varied from 10 mN/min to 500 mN/min. The blends which contained very low % PI (8 %, and 17 %) are brittle and were not measured. Only the blends which contained % PI higher than 25 % were measured in this mode.

In this measurement, the effects of composition ratio on the Young's modulus and the strain rate were studied.