CHAPTER II
EXPERIMENTAL SECTION

2.1 Materials

Polyisoprene (PI), polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene) (PPO) were used as homopolymers, and poly(isoprene-b-styrene) (P(I-b-S)) was used as a compatibilizer in this work. In this study we examined two ternary blends. The ternary blends systems comprise of a PS/P(P-b-I)/PI system and a PPO/P(S-b-I)/PI system.

The polyisoprene (PI) was a commercial product of the Japan Synthetic Rubber Co., Ltd. The laboratory grade polystyrene (PS) was purchased from Polyscience, Inc. The molecular weight of PS was given from the supplier as 50,000. The laboratory grade poly(2,6-dimethyl-1,4-phenylene) (PPO) was purchased from Polyscience, Inc. which has a quoted molecular weight of 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), with $M_w/M_n = 1.06$.

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

The analytical grade chloroform, used as the solvent for poly(2,6-dimethyl-1,4-phenylene)/polyisoprene solutions was purchased from Ajax Chemical.

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2.3 Sample Characterizations

2.3.1 Molecular Weight Determination

The molecular weight of Polyisoprene (PI) was determined by using the Mark-Houwink equation :

$$[\eta] = KM_v^a.$$
(2.1)

where $[\eta]$ is intrinsic viscosity, M_v is the viscosity average molecular weight, and K and a are constants. The constants K and a can be obtained empirically for given polymer, solvent and temperature. From W.H. Beattie and C. Booth (1963) for PI in toluene at 30 °C, the constants K and a are 2.00 x 10^{-3} (ml/g) and 0.728 respectively. So

$$[\eta] = 2.00 \times 10^{-3} M_v^{0.728}.$$
(2.2)

Intrinsic viscosity, $[\eta]$ was obtained from an extrapolation of the specific viscosity, η_{sp} devided by the concentration, C_p to zero concentration as shown in Figure 2.1. We obtained intrinsic viscosity, $[\eta]$, of 440.81 ml/g. Thus the viscosity average molecular weight of PI is 9.25x10^5.
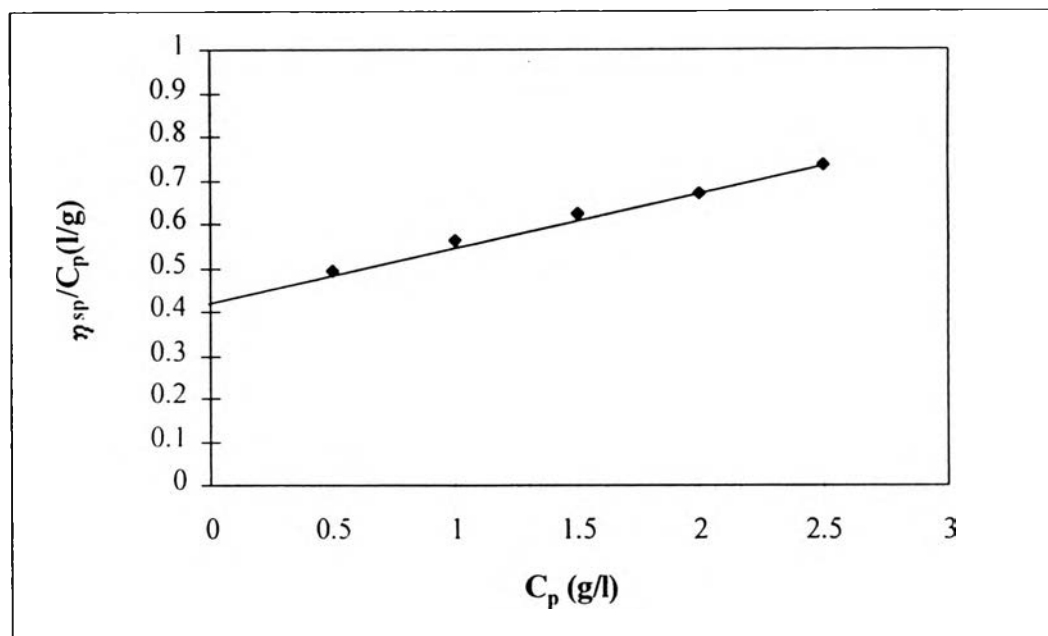
Figure 2.1 Schematic of a plot of η_{sp}/C_p and extrapolation to zero concentration to determine $[\eta]$. The polymer was PI.

2.3.2 Glass Transition Temperature Determination

Glass transition temperature (T_g) at onset of PI, PS and PPO were measured by Differential Scanning Calorimeter (DSC), model TASC 414/3 from NETZCH with a heating rate 10 °C/min. We obtained the following T_g's :

Table 2.1 T_g of the three polymers

| Polymer	T_g (°C)
PI	-62.8
PS	72.8
PPO	212.5

2.4 Instrument and Measurement

2.4.1 Parallel Plate Rheometry

A parallel plate rheometer, Rheometric Scientific (model RES), was used to obtain T_α of our samples.

Principle

The rheometer measures G', G'' and Tanδ where the sample undergoes repeated small-amplitude strains in a cyclic manner. Molecules perturbed in this way store a portion of the imparted energy elastically and dissipate a portion in the form of heat. The quantity, G', shear storage modulus, is a measure of the energy stored elastically, whereas G", shear loss modulus, is a measure of the energy loss as heat. Tanδ is called the loss tangent (tanδ = G''/G'). δ being phase lag between the input strain and output stress. Tanδ also goes through a series of maxima. The maxima in G" and tan δ are sometimes used as the definition of T_α. For the α-transition, the portion of the molecule excited comprises from 10 to 50 atoms or more (Brandruys and Immergut, 1975).

The dynamic mechanical behavior of an ideal polymer is illustrated in Figure 2.2. The storage modulus generally follows the behavior of Young's modulus. The quantities G" and tanδ display maxima at T_α, the tanδ maximum usually appears several degrees centigrade higher than the G" peak. Also shown in Figure 2.2 is the β peak generally involving a smaller number of atoms. The area under the peaks, especially when plotted with a linear y axis, is related to the chemical structure of the polymer. The width of the transition and shifts in the peak temperatures of G" or tanδ are sensitive guides to the exact state of the material, molecular mixing in blends, and so on (Sperling, 1993).
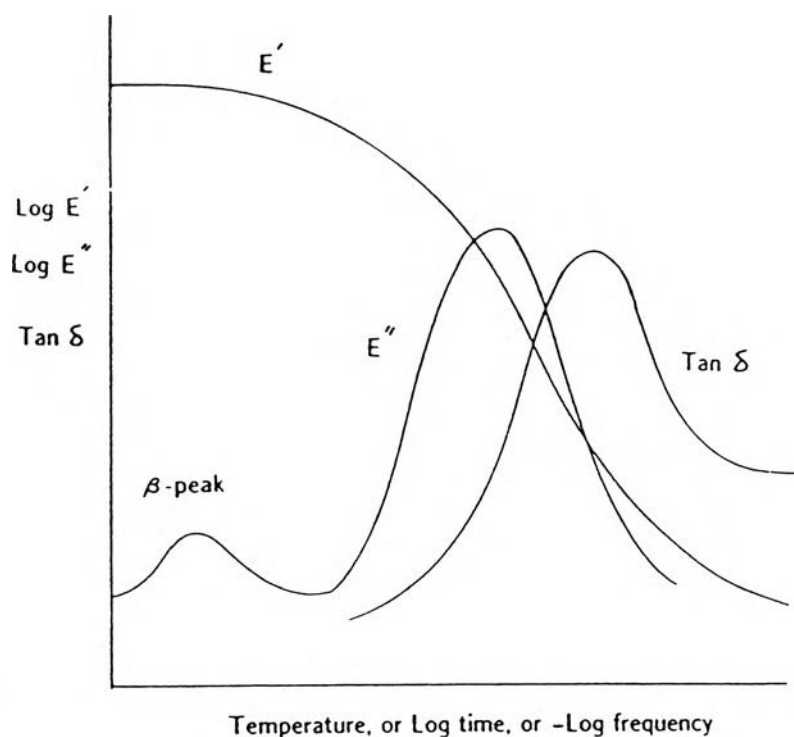
Figure 2.2 The dynamic mechanical behavior of an ideal polymer.

Procedure

The sample film was cut into a dish shape of 25 mm in diameter and 0.4-0.5 mm in depth. Strain sweep experiment was performed at constant ω and T to ensure linear viscoelasticity behavior in which G' and G" are independent of strain. From this experiment at constant ω (1 Hz) and T (30 °C), a small strain value in the linear viscoelastic range (0.0-0.6%) was chosen. The samples were measured by a parallel plate (Diameter 25 mm) in the dynamic temperature ramp mode. The temperature was from -80 °C to 150 °C for PS/P(S-b-I)/PI blends and -80 °C to 300 °C for PPO/P(S-b-I)/PI blends with a rate of 5 °C/min, a frequency of 1 Hz and a small strain. Low temperature(-80-25°C) was attained by a cooling with the liquid nitrogen. High temperature (25-300°C) was attained by a controlled air heater.

2.4.2 Dynamic Mechanical Analysis (DMA)

The DMA apparatus is the model 7-e from Perkin-Elmer. In this study, we used the extensional analysis system in the creep/recovery mode which was used to obtain the Young's modulus, strain rate and yield stress.

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 as shown in Figure 2.3.
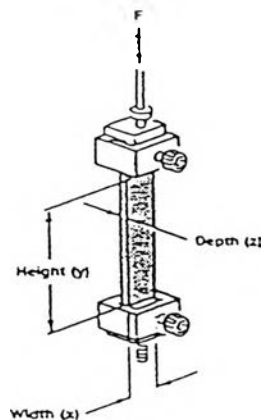
Figure 2.3 Extension Analysis Measuring System: Stainless Steel Parallel Clamp.

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 the strain is monitored.

Procedure

The dimension of samples were rectangular with 3.0 mm in width, 3.0 mm in height and 0.4-0.5 mm in depth. Dynamic Mechanical Analysis (DMA-7e) was used with the extension probe in the creep/recovery mode. A force rate of 500 mN/min was applied for the Young's modulus and the strain rate measurement. We used the highest force rate (500 mN/min) to minimize relaxation of the samples. A minimum force rate of 10 mN/min was applied for the yield stress measurement is small force rate. During extension, there was enough time for the chain molecules to relax and we obtained an equilibrium stress-strain curve.

Calculations

Young's Modulus, E was obtained from the initial slope of stress and strain curve :

$$E = \sigma/\varepsilon, \qquad (2.3)$$

where E is Young's modulus (Pa), σ is stress (Pa), and ε is strain.

Strain rate in the linear elastic regime, $\dot{\varepsilon}$ was determined from :

$$\dot{\varepsilon} = (\delta\sigma/\delta t)/E, \qquad (2.4)$$

where $\dot{\varepsilon}$ is strain rate, $\delta\varepsilon/\delta t$ is stress rate (Pa.min^{-1}), and E is Young's modulus (Pa).

Strain rate in the nonlinear regime was determined from :

$$\dot{\varepsilon} = \dot{\varepsilon}_V + \dot{\varepsilon}_E + \dot{\varepsilon}_{IN}, \qquad (2.5)$$

where $\dot{\varepsilon}_{IN}$ is strain rate induced by interfacial interaction at the interface, $\dot{\varepsilon}$ is total strain rate, $\dot{\varepsilon}_V$ is strain rate of viscous part and $\dot{\varepsilon}_E$ is strain rate of elastic part. The strain rate of each part is illustrated in Figure 2.4.
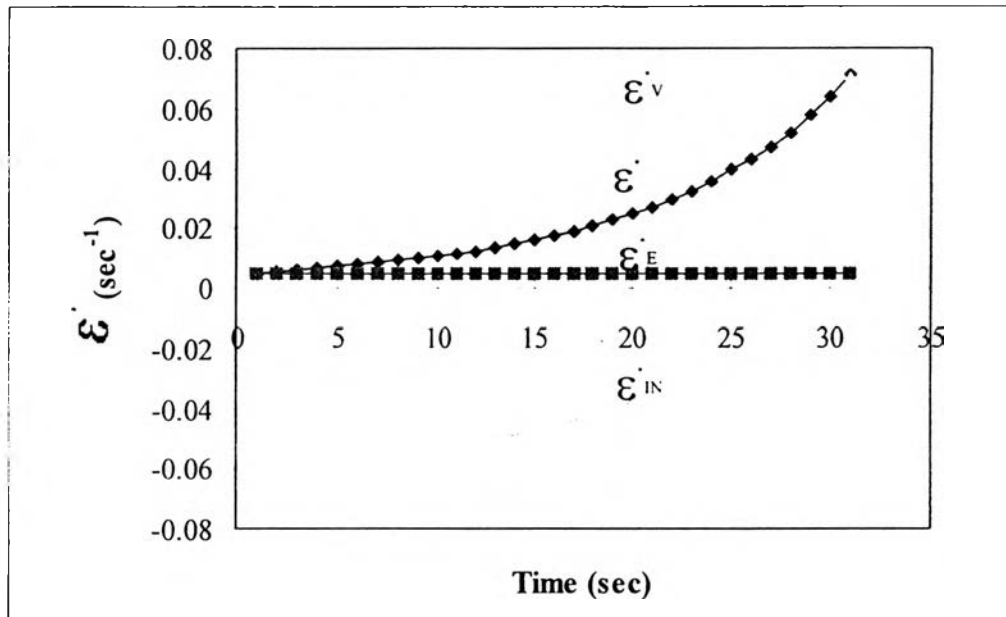
Figure 2.4 Strain rate of each part in the nonlinear regime.

The strain rate was obtained numerically from the strain vs. time curve as follow :

by $\qquad\qquad\qquad \dot{\varepsilon} \cong (\dot{\varepsilon}_{i+1} - \dot{\varepsilon}_{i-1})/2\Delta t,$ $\qquad\qquad$ (2.6)

Δt was calculated from $\qquad \Delta t = t_{i+1} - t_i,$ $\qquad\qquad\qquad$ (2.7)

and $\qquad\qquad\qquad\qquad t = 1/\omega,$ $\qquad\qquad\qquad\qquad$ (2.8)

then $\dot{\varepsilon}_v$ was calculated from $\qquad \dot{\varepsilon}_v = \sigma/\eta',$ $\qquad\qquad\qquad$ (2.9)

η' was obtained from $\qquad\qquad \eta' = E''/\omega,$ $\qquad\qquad\qquad$ (2.10)

and $\qquad\qquad\qquad\qquad \dot{\varepsilon}_E = \dot{\sigma}/E ,$ $\qquad\qquad\qquad$ (2.11)

where σ is stress, η' is viscosity, E'' is loss modulus, ω is the frequency, $\dot{\sigma}$ is stress rate, E is Young's modulus and t is transient time.

Yield stress, σ_y is the 0.2% offset yield stress that was obtained from the initial slope of the stress strain curve with a line parallel to this which is offset by 0.2 % from the origin. The reader may glance at Figure 2.5 for the definition and determination of the yield stress.
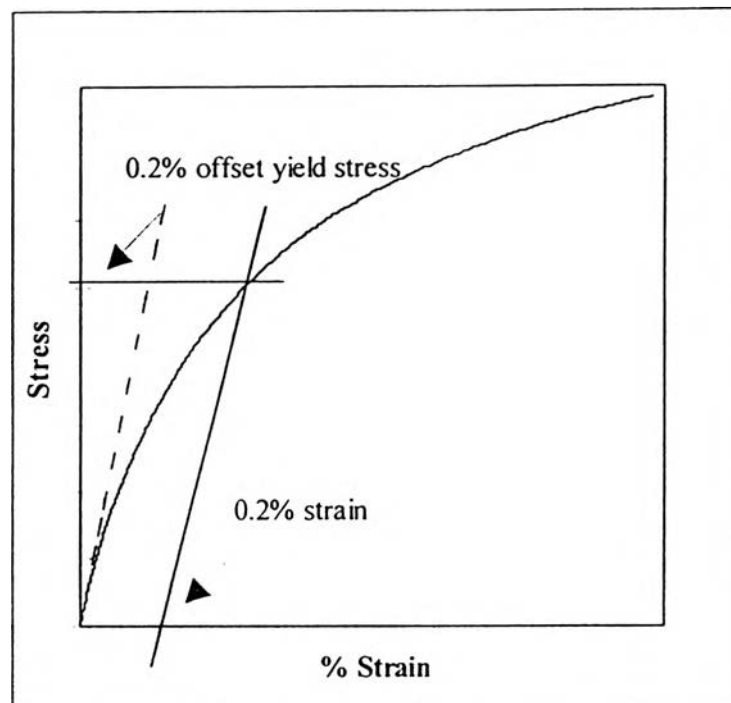
Figure 2.5 0.2% offset yield stress on the stress-strain curve.

2.4.3 Scanning Electron Microscopy (SEM)

SEM, JEOL 5200-2AE (MP152001) with a magnification range of 35-200,000 times, was used to observe fracture surface morphology of our samples.

Procedure

The sample film was fractured in a liquid nitrogen. For coating samples, the samples were mounted on stubs on the sputting device. The samples were coated with sputtered gold for 3 min. Coated sample morphology was observed by SEM at an accelerating voltage of 20 kV and magnification of 2000.